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THE φ-SCALE OF POTENTIAL AND ITS APPLICATION TO SOME ELECTROCHEMICAL PROBLEMS. PART II. INVESTIGATION OF INHIBITION ACTION OF ORGANIC COMPOUNDS

By L. I. Antropov* and S. N. Banerjee

In the present paper, φ-scale of electrode potentials has been utilised in the investigation of mild steel corrosion inhibition in acidic solutions with different types of organic compounds as inhibitors. It was found that φ-scale of potentials gave a possibility for the electrocapillary data to be used both for qualitative and quantitative study of inhibitors' action. For example, it proved possible to determine, by means of electrocapillary curves, the alteration of inhibitors' efficiency with the change in their concentfation. Several further applications of this method have been discussed. It has been shown also that φ-scale of potentials gives a basis for elucidation of the main condition under which any other indirect methods (differential capacity measurements, suppression of polarographic maxima, etc.) can lead to the results comparable with the direct estimation of decrease of corrosion rate due to inhibitors' influence.

In the first paper of this series (Antropov, this *Journal*, 1958, **35**, 309), a new scale of electrode potential, φ-scale, in which the null-point of metal is chosen as the basis, has been discussed (see also Antropov, *J. Phys. Chem., USSR.*, 1951, **25**, 1494 ; *Proc. Electrochem. Cong.*, 1953, 380, Moscow ; *Uspechy Chimii, USSR.*, 1956, **25**, 1043 et seq). It has been shown that, when for two different metals, M_1 and M_2, the values of φ-potentials are equal ($_{M_1}\varphi = {}_{M_2}\varphi$), their charges and the conditions of physical adsorption on the surface of these metals in contact with solutions are also similar. This provides a possibility of comparing the data obtained for different metals, when the criterion mentioned above is fulfilled. It can also be utilised in the study of corrosion inhibition in acidified solutions, where different types of organic compounds are used as inhibitors. This inhibition action is probably connected with the physical adsorption on metal—solution interface, and therefore depends on the charge of metal with respect to the solution. The most direct evidence, and the quantitative characteristic of adsorption from solutions at different potentials, can be obtained by means of electrocapillary curves. In the present paper this method has been used, and its results have been compared with those of corrosion experiments, taken from literature sources.

*Present address : Indian Institute of Technology, Bombay.

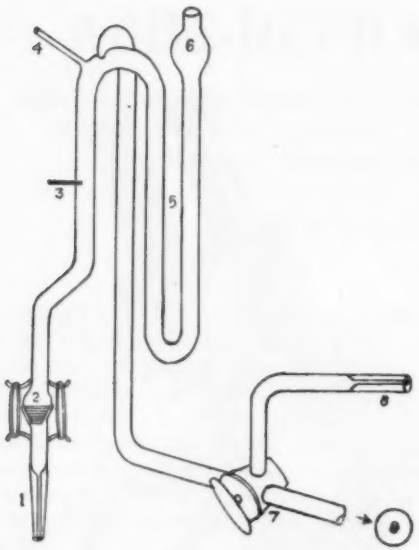
EXPERIMENTAL

Electrocapillary curves have been obtained by means of a capillary electrometer (Fig. 1). It differs from the usual type only by the process of producing the pressure. The necessary pressure can be reached by means of a small rubber bladder, and the excess can be removed by means of a thin glass tube connected with the three-way stop-cock. The capillary can be easily replaced, for there is a ground-glass joint, introduced in this modified form. Potentials are read from a Cambridge portable potentiometer. The values of surface tension (σ) have been calculated from the equation:

$$\sigma = \tfrac{1}{2}\, g r\, \rho_{Hg}\, (h_1 - h_2 + h_M) \quad \ldots \quad (1)$$

where r is the radius of the capillary, h_1, the height of mercury column, h_2, the height of the position of Hg inside the capillary from capillary tip, h_M, the difference in heights of mercury in the manometric tube of the electrometer, ρ_{Hg}, the density of mercury and g, the acceleration due to gravity = 978.2 dynes/cm^2.

FIG. 1

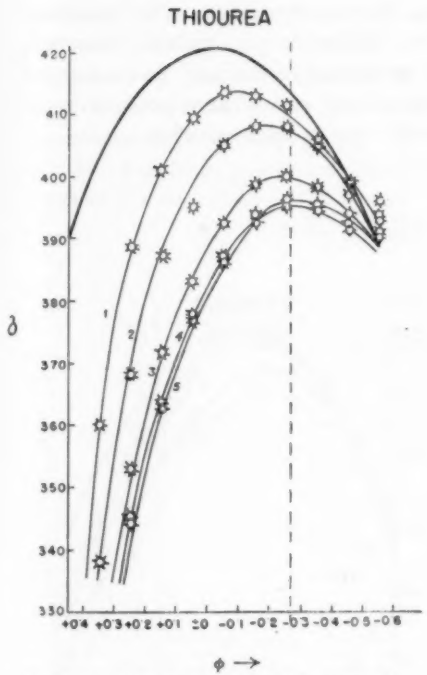


(1) Capillary. (2) Ground-glass joint. (3) Platinum wire (sealed), electric connection. (4) Mercury filling tube. (5) Manometric tube. (6) Reservoir for mercury. (7) Three-way cock. (8) Glass capillary for excess pressure removal. (9) Rubber bladder (for producing pressure) (not shown in the fig.).

Before each experiment, a few droplets of mercury were pumped out to provide a fresh surface of mercury. The surface, thus obtained, was kept in contact with the solution of an organic compound in 1N-H_2SO_4 for nearly $\frac{1}{2}$ hour to reach an equilibrium. All experiments were carried out at room temperature ($25° \pm 2°$) and a 1N-H_2SO_4 solution (Analar) in bidistilled water (to avoid possible contamination by surface active materials) was used. The organic compounds with their respective grades, selected for this electrocapillary experiments, are: thiourea (A. R.), diethylamine (B.D.H.-L.R.), aniline (Nadia Chemical, L.R.), quinoline (B. D. H. - L.R.), β-naphthoquinoline (B.D.H. – L.R.) and pyridine (Analar, distilled).

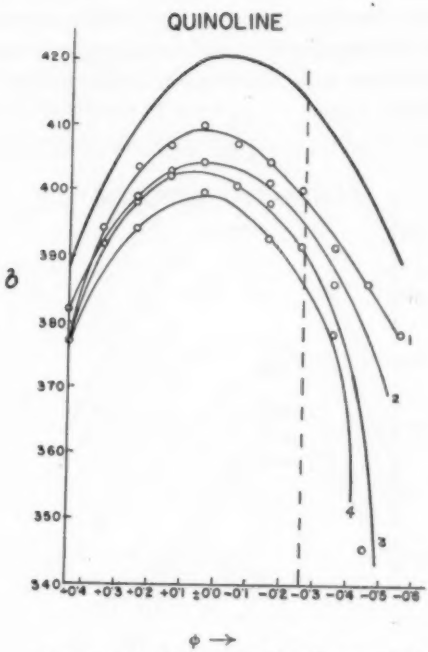
For all these compounds, the variation of the inhibition action with concentration is given in the literature. For some of them (vide Fig. 9), the electrocapillary curves were obtained previously, and therefore a comparison of our results with those of others was possible.

FIG. 2



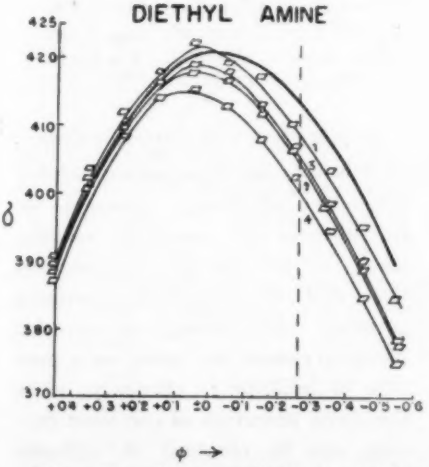
Curves 1-5 refer respectively to 0.0104 *M*, 0.038 *M*, 0.086 *M*, 0.140 *M* and 0.184 *M* solns. in 1*N*-H_2SO_4. Solid line curve refers to 1*N*-H_2SO_4.

FIG. 3



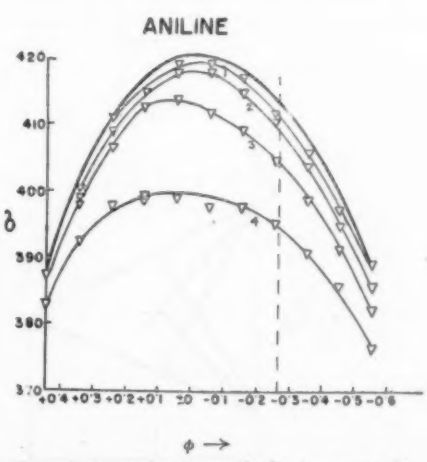
Curves 1-4 refer respectively fe 0.00196 *M*, 0.00796 *M*, 0 107 *M* and 0.030 *M* solns. in 1*N*-H_2SO_4. Topmost curve refers to 1*N*-H_2SO_4.

FIG. 4



Curves 1-4 refer respectively to 0.816 *M*, 0.309 *M*, 0.424 *M* and 0.548 *M* solns. in 1*N*-H_2SO_4. Solid line curve refers to 1*N*-H_2SO_4.

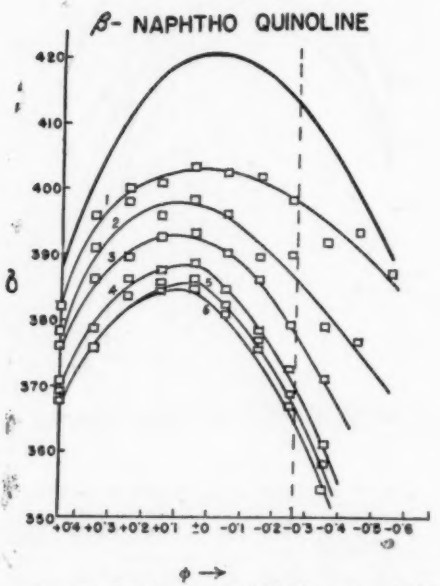
FIG. 5



Curves 1-4 refer respectively to 0.0101 *M*, 0.0385 *M* and 0.126 *M*, 0.295 *M* solns. in 1*N*-H_2SO_4. Topmost curve refers to 1*N*-H_2SO_4.

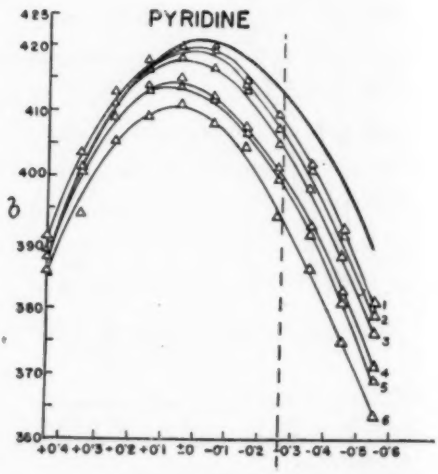
The electrocapillary curves are shown in Figs. 2 to 7. They covered usually a wide range of inhibitor's concentration. It can be seen from these curves that thiourea functions as a surface-active anion, while diethylamine, aniline, quinoline, β-naphthoquinoline and pyridine act mainly as surface-active cations. In the cases of quinoline and β-naphthoquinoline, the electrocapillary curves at φ-potential more negative than $-0.35 \div -0.45$ are distorted, apparently due to their reduction.

FIG. 6



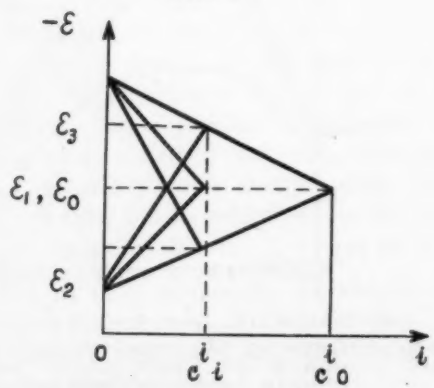
Curves 1-6 refer respectively to 0.0000583 *M*, 0.000226 *M*, 0.000723 *M*, 0.00206 *M*, 0.00347 *M* and 0.00589 *M* solns. in 1*N*-H_2SO_4. Top curve refers to 1*N*-H_2SO_4.

FIG. 7



Curves 1-6 refer respectively to 0.0293*M*, 0.0607 *M*, 0 101 *M*, 0.280 *M*, 0.419 *M* and 0.558 *M* solns. in 1*N*-H_2SO_4. Top most curve refers to 1*N*-H_2SO_4.

FIG. 8



Comparison with Corrosion Data

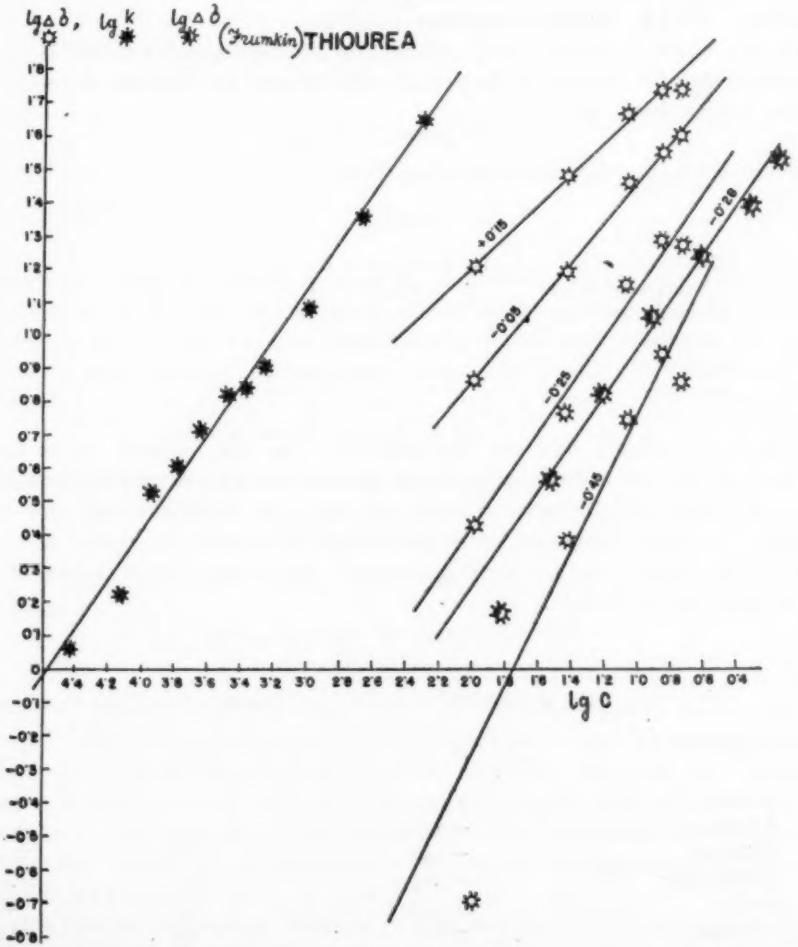
Principle of Comparison.—Addition of increasing amounts of an inhibitor to corrosion medium results in (*a*) decrease of corrosion rate, and (*b*) change of corrosion potential. The change of corrosion potential cannot be taken as a measure of inhibitor's efficiency, since the same reduction of corrosion current can be obtained at different values of corrosion potential (vide Fig. 8). It depends first of all on

the effect, which an inhibitor exerts on the polarisation of cathodic and anodic processes. The change of corrosion potential due to addition of organic compounds is normally small, and < 0.1 volt. Therefore, for all calculations made in this paper, the corrosion potential of iron in H_2SO_4 in presence of organic compounds is taken as a constant value of -0.28 volt against standard hydrogen electrode, in accordance with literature data.

The null-point of iron is equal to -0.02 volt, and therefore the corrosion potential given in φ-scale will be

$$_{Fe}\varphi_{Cor} = -0.28-(-0.02) = -0.26 \text{ volt.}$$

FIG. 9



The most accurate value of null-point of mercury seems to be -0.19 volt, but in most cases, including the given case, the maximum point in electrocapillary curve

in $1N$-H_2SO_4 corresponds to a potential of -0.21 volt, which therefore has been chosen as the null-point of mercury. A similar behaviour of the same organic compound in both corrosion and electrocapillary experiments can be obtained only at the same value of φ-potential. In the present case, the φ-potential equal to $_{Hg}\varphi_{e.c.c.} = -0.26$ (where e. c c. = electrocapillary curve) is indicated in Fig. 2-7 by dotted line.

Results of Comparison.—The data obtained by Ride (*J. Electrochem. Soc.*, 1956, **103**, 98) have been used for comparison. These data correspond to corrosion of iron in $1N$-H_2SO_4 at 25°. For thiourea, the data were taken from Hoar and Holliday's paper (*J. Appl. Chem.*, 1953, **3**, 502). These data were obtained at 70°, but usually the values of inhibition coefficient, *i.e.* $K_1 = i_o/i_1$ (i_o and i_1 are rates of corrosion in absence and in presence of inhibitors respectively) vary with temperature not to a great extent, and a comparison is therefore possible.

The plot of log K_1 against log C, where C is the concentration of inhibitor, results in a series of straight lines (see Figs. 9 to 11) with different values of the slope.‡

The empirical relation,

$$\log K_1 = \text{const}_1 + \beta_1 \log C \quad \ldots \quad \ldots \quad (2)$$

is true with the values of constants shown in Table I.

TABLE I

Thiourea	... ...	log K_1	$= 3.31 + 0.72 \log C$
β-Naphthoquinoline	...	,,	$= 1.52 + 0.31$,,
Diethylamine	... ...	,,	$= 0.83 + 0.36$,,
Quinoline	... ...	,,	$= 0.83 + 0.29$,,
Aniline	... ...	,,	$= 0.70 + 0.61$,,
Pyridine	... ...	,,	$= 0.55 + 0.33$,,

The electrocapillary data are represented in the same figures. It is also seen that in this case an approximately linear relation exists between log $\Delta\sigma$ and log C. The slope of these straight lines varies with the nature of compound and the value of potential. For each compound it is possible to find a value of potential at which the slopes of log K_1—log C and log $\Delta\sigma$—log C curves are equal. These values of potentials are recorded in Table II.

TABLE II

Compounds.	Value of φ-potential at which $\frac{\log \sigma\Delta}{\log C} = \frac{\log K_1}{\log C}$.	Constants of eq. (3) at ε=0.71 volt (φ = − 0.26 V).	
		Const_2	β_2.
Thiourea	− 0.23	1.63	0.74
β-Naphthoquinoline	− 0.25	2.34	0.29
Quinoline	− 0.26	1.76	0.29
Diethylamine	− 0.23	1.15	0.41
Aniline	− 0.29	1.46	0.64
Pyridine	− 0.27	1.34	0.37

‡The graphical representation is shown here only for thiourea, quinoline and pyridine; for other compounds only the results of calculations based on the similar graphs are given.

FIG. 10

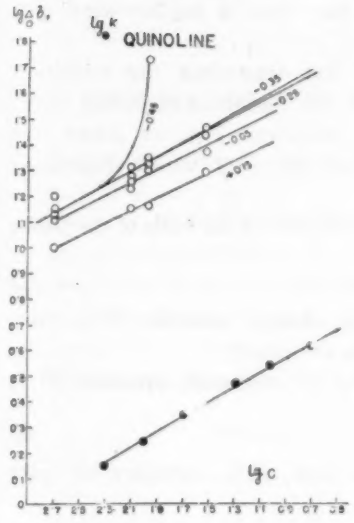
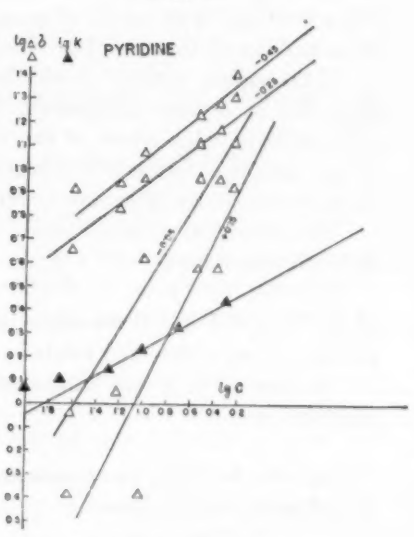


FIG. 11



The average value of potential at which the coincidence of the slopes is observed is equal to -0.255 V. Within the limits of experimental errors, it corresponds to the corrosion potential (-0.26) given in φ-scale. Hence, for the relation between $\Delta\sigma$ and C existing at the same potential as the corrosion potential in φ-scale, the equation (3) can be written as

$$\log \Delta\sigma = \text{const}_2 + \beta_2 \log C \quad \ldots \quad (3)$$

where β_2 is approximately equal to β_1 of equation (2).

DISCUSSION

From empirical equations (2) and (3), assuming that $\beta_1 = \beta_2$, the following relations can be obtained:

$$\log K_1 = \text{const}_1 - \text{const}_2 + \log \Delta\sigma$$

or

$$\log K_1 = \text{const}_3 + \log \Delta\sigma \quad \ldots \quad \ldots \quad (4)$$

This equation indicates that inhibition coefficient is a function of surface activity. This relation ought to be expected because the influence of organic inhibitors is usually a result of their adsorption on metal—solution interface. But here the inhibition coefficient and adsorption are estimated for one and the same compound, but for two different metals. The equation (4) can be true when $\beta_1 = \beta_2$, and it takes place only when these two metals (in this particular case, iron and mercury) have the same value of φ-potential (here ${}_{Fe}\varphi_{Cor} = {}_{Hg}\varphi_{e.c.e.} = -0.26$ V).

It means that the adsorption isotherm is within some limits independent of the nature of metal, if the process of adsorption is considered at the same value of φ-potential. At the same time, if this condition is not fulfilled, the data obtained for one metal could not be used for any suggestions concerning the process of adsorption

on other metal. So, for example, if iron and mercury be taken at the same potential in hydrogen scale ${}_{Hg}\epsilon_{s.c.e.} = {}_{Fe}\epsilon_{Cor} = -0.28$ V, then the slope of $\log\Delta\sigma$—$\log C$ will be quite different from the slope of $\log K_1$—$\log C$.*

If the surface activity would be the only factor that determines the inhibition properties of organic compounds, then at the given φ, the inhibition coefficient ought to be similarly independent of the nature of organic particles. Fig. 12 shows that surface activity is certainly very important, but not the sole property which determines the inhibition action of organic compounds.

The empirical relation between $\Delta\sigma$ and C can be derived on the basis of the Gibbs adsorption equation :

$$d\sigma = -qd\epsilon - \Sigma RT\Gamma\, d\ln C \qquad \ldots \quad (5)$$

where, σ, q, ϵ, Γ and C are respectively interface tension, charge, potential of mercury surface, excess surface and volume concentration of each compound.

In case of only one compound (organic inhibitor of corrosion), equation (5) is simplified to

$$d\sigma = -qd\epsilon - RT\Gamma\, d\ln C \qquad \ldots \quad (6)$$

In order to obtain an agreement with experimental data, it is necessary to make the following assumptions :

(1) The potential remains constant : $d\epsilon = 0$.

(2) The excess concentration is equal to the surface concentration : $\Gamma = C'$.

(3) The latter is a Freundlich's type function of volume concentration :

$C' = {}_{Hg}K_1C^{\beta}$ then, from (6) and above,

$$d\sigma = -RT\,{}_{Hg}K_1C^{\beta}\, d\ln C$$

or after integration, $\sigma = \dfrac{-RT}{\beta}\,{}_{Hg}K_1C^{\beta} + \text{const.}$

with C equal to 0, $\sigma = \sigma_0$;

hence the integration constant must be equal to $+\sigma_0$. Then,

$$\sigma_0 - \sigma = \Delta\sigma = \frac{RT}{\beta}\,{}_{Hg}K_1C^{\beta} \qquad \ldots \qquad \ldots \quad (7)$$

or, $$\log\Delta\sigma = \log\frac{RT}{\beta}\,{}_{Hg}K_1 + \beta\log C = \text{const}_2 + \beta\log C. \qquad \ldots \quad (8)$$

The empirical formula (2) can be derived by many ways. So, it can be assumed that the energy of activation of rate-determining stage of corrosion process is a linear function of $\ln C'\gamma$, γ being a factor connected with size and other specific properties of inhibitor particles. In presence of an inhibitor, the equation of corrosion rate

$$i_{Cor} = \text{const.}\; e^{-\frac{\alpha\epsilon_1 F}{RT}} \qquad \ldots \qquad \ldots \quad (8)$$

will be transformed to

$$i_{Cor} = \text{const.}\; e^{-\frac{\alpha\epsilon_2 F + RT\ln C'\gamma}{RT}}$$

* This value of potential corresponds to ${}_{Hg}\phi = -0.28 - (-0.21) = -0.07$ V and to ${}_{Fe}\phi = -0.28 - (-0.02) = -0.26$ V and the main condition of comparison (${}_{Fe}\phi = {}_{Hg}\phi$) is not fulfilled.

and the inhibition coefficient will be represented as :

$$_{Fe}K_I = \frac{i_{Cor}}{i'_{Cor}} = e^{\frac{\alpha(\epsilon_2-\epsilon_1)F+RT\ \ln C'\gamma}{RT}} \quad \ldots \quad \ldots \quad (9)$$

In many cases it is possible to neglect the change of potential, and (9) reduces to

$$_{Fe}K_I = C'\gamma. \quad \ldots \quad \ldots \quad (10)$$

If the Freundlich formula is valid for the system under investigation then,

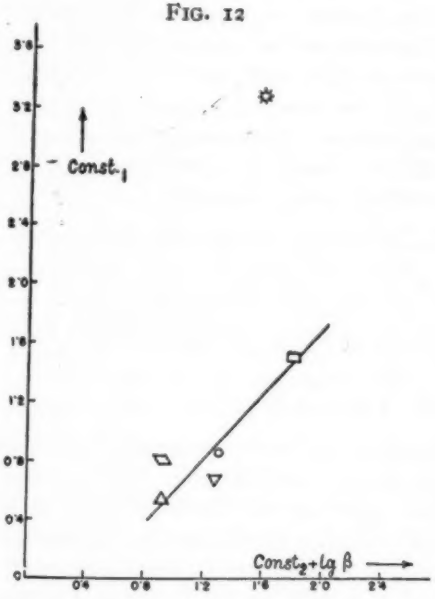
$$_{Fe}K_I = {}_{Fe}K_f C^{\beta}$$

or, $$\log K_I = \log {}_{Fe}K_f\gamma + \beta \log C = \text{const.}_1 + \beta \log C. \quad \ldots \quad (11)$$

Frome quations (7) and (11) it is seen that the const$_2$ is a function of K_f for mercury and β, while the const.$_1$ is a function of K_f for iron (or any other metal under comparison) and γ. Both of these constants are, hence, functions of the nature of metal and organic compound.

Therefore, it is natural to expect that these two constants also ought to satisfy one another in a functional relation. If the specific constant β will be excluded from const$_2$ by adding the corresponding values of logβ, then for two given metals and for similar compounds, this relation ought to be of a simlar type. Fig. 12 represents the relation between const$_1$ and (const$_2$ + log β).

FIG. 12



The experimental points for pyridine, quinoline and β-naphthoquinoline are lying on the same straight line with a value of slope very near to 1. The points for aniline and diethylamine are in the vicinity of this straight line, but the point corresponding to thiourea is remote from it. It is seen therefore that the inhibition action depends on (*a*) the surface activity of compound at the potential of corrosion, (*b*) on the size of particles in a given homologous series and (*c*) on the nature and number of surface active groups.

Application of the Method

Though these investigations are very far from being completed, many different applications of the method can be foreseen*.

* The idea of this method was formulated first by L. I. Antropov in a paper delivered at a Corrosion Congress (Moscow, Dec., 1955). Further development of this idea has been given by A. T. Petrenko (Thesis, Novotcherkassk, 1956) and V. P. Grigoriev (Thesis, Novotcherkassk. 1958). Their results are in a good agreement with those described in the present paper. Various applications of electrocapillary measurements and of ϕ-scale to corrosion of metals were considered in 1954-55 (Antropov, *Trans. Novotcherkassk Polytech. Inst.*, 1954, **25/39**, 5; *Proc. V Corrosion Cong.*, 1955, 79, Moscow).

1. The coincidence of slopes of $\log K_i - \log C$ and $\log \Delta\sigma - \log C$ straight lines is observed at the potential of mercury equal to corrosion potential in φ-scale, which allows to predict the change of inhibitor's action with concentration. Really, if one value of inhibition coefficient is known, the values of K_i at any other concentration can be calculated by means of equation (2), using the value of β taken from electrocapillary measurements.

2. It is possible to predict the variation of inhibitor's action when the conditions of corrosion are changed. This can be illustrated by two examples:

(*a*) If the corrosion of iron will occur not in a pure sulphuric acid solution, but in the same solution containing some oxidising agent (ferric ions, potassium dichromate etc.), the value of corrosion potential will be changed in the positive direction. Let the new value of corrosion potential be equal to + 0.3 V in φ-scale. Then the surface activity of organic compounds ought to be estimated not at −0.26 V, as it was made in case of pure acid solution, but at + 0.3 V. The consideration of electrocapillary curves shows that here most of the cationic-like organic compounds (such as aniline, pyridine, quinoline etc.) will be removed from the surface of corroding metal, and therefore they cannot be effective as inhibitors of corrosion. This fact* was stated by Elze and Fisher (*J. Electrochem. Soc.*, 1952, **99**, 259), who offered, however, a different explanation. On the other hand, anion-like compounds (e.g. thiourea) ought to be more effective, because their surface concentration will be increased. The change of inhibition action of molecular compounds will depend on their polar properties.

(*b*) It is well known that many attempts to find an effective inhibitor for prevention of Zn or Al corrosion in alkaline solution have failed. The reason of these unsuccessful searches is connected most probably with the highly negative values of corrosion potentials both for Zn and Al. So, the corrosion potential of Al in φ-scale is not $< \varphi_{Cor} = -1.1$ V.

$$[{}_{Al}\varphi_{Cor} = {}_{Al}\varphi_{Cor} - {}_{Al}\varepsilon_{q=0} = -1.5 - (-0.4) = -1.1 \text{ V}]$$

When these values of φ-potential are reached, the surface concentration of anions and anionic-like organic compounds ought to be very near to zero. The surface-active cations are replaced in the electric double layer by the smaller cations of alkali. The surface-active compounds of molecular nature are also withdrawn from the metal—solution interface by water molecules.

3. This method can be used for investigation of inhibition activity of different functional groups. If, as it was stated in the case of pyridine compounds, a simple relation between constants of equations (2) and (3) be found for other types of organic substances, the method can ofer the possibility of calculation of inhibition activity only from electrocapillary measurements.

4. This method allows to formulate the conditions under which the application of many other methods, used for investigation of inhibition action, may lead to the positive results.

* Another reason for cessation of inhibitor's action may be connected with the fact that the kinetic limitations have been changed for the diffusion ones.

The capacity of electric double layer can be a measure of the surface activity of organic compounds. These data can be obtained with higher degree of accuracy only in case of mercury electrode. Because the adsorbability and, consequently, the differential capacity are functions of potential ; only those values of capacities can be taken into consideration which correspond to the potential of mercury electrode equal to the potential of corroding metal given in the φ-scale.

The results of direct estimation of adsorption of different organic compounds from non-aqueous solution on the surface of metal under investigation cannot be quantitatively compared with the inhibition activity of the same compounds. The values of potentials in these two series of experiments (estimation of amounts of adsorbed particles and estimation of the magnitude of inhibition) can be very different. The different nature of solvents in case of adsorption and corrosion measurements can also distort the real state of things.

The suppression of polarographic maxima can be a measure of inhibition activity only when the position of maxima corresponds to the potential of corrosion given in the φ-scale (cf. Gatos, *J. Electrochem. Soc.*, 1954, **101**, 433).

In the special case of iron corrosion in $1N$-H_2SO_4, the position of maximum ought to be near to -0.26 V in φ-scale. Neither oxygen, nor lead and nickel maxima correspond to this condition. The potential of nickel maximum ($_{Ni}\varphi_{max} = -1.30 + 0.28 + 0.21 = -0.81$) is more negative than the corrosion potential, and the surface activity of cations will be increased and that of anions will be diminished in comparison with the adsorption of the same compounds on the surface of corroding iron. Better agreement can be expected only in case of organic compounds of molecular type. The potential of oxygen and probably of lead maxima are more positive than the value of corrosion potential of iron given in φ-scale. Therefore the condition of adsorption ought to be inversed with respect to nickel maximum.

All these methods, including electrocapillary curves method, can furnish under appropriate conditions the magnitude of adsorption of organic compounds on the surface of corroding metal. The surface activity is very important but, as it has been indicated above, it is not the single property of organic compound which alone determines its inhibitory action. The nature of these still-unknown properties may be hoped to be found as a result of systematic, comprehensive and relative study of adsorption of different organic compounds and their inhibition efficiency.

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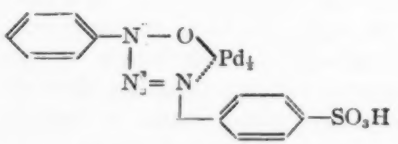
SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF METAL COMPLEXES OF 3-HYDROXY-1-*p*-SULPHONATOPHENYL-3-PHENYL-TRIAZINE. PART I. PALLADIUM COMPLEX

By Umesh Chandra Durgapal and N. C. Sogani

Palladium forms an intensely yellow-coloured, water-soluble complex with 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine. The formula of the complex, established spectrophotometrically by applying Job's method, slope ratio method and molar ratio method and also conductometrically, has been determined to be PdR_2 (R=reagent) The molecular extinction coefficient has been found to be 18.75×10^3 at 425mμ. The dissociation constant at 25° has been found to be 3×10^{-12} and free energy of formation of the complex is −15.72Kcal./mole.

Recently Sogani and Bhattacharyya (*Anal. Chem.*, 1957, **29**, 397) have reported the use of 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine as an excellent colorimetric reagent for palladium. The reagent and the metal complexes given by it are water-soluble. The colour development with palladium is almost instantaneous and the intensity remains unaltered even after 24 hours. The system is stable under wide ranges of p_H and temperature variation. The reagent and the palladium complex have well-separated absorption peaks so that the excess of the reagent does not interfere in the photometric estimations.

The present investigation was undertaken with a view to establishing the formula of palladium-3-hydroxy-1-*p*-sulphonatophenyl - 3 - phenyltriazine complex, using spectrophotometric and conductometric methods. In spectrophotometric method, we have adopted Job's method of continued variation (*Compt. rend.*, 1928, **180**, 928 ; *Ann. chim.*, 1928, *x*, **9**, 113), slope ratio method (Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488) and molar ratio method (Yoe and Jones, *Ind. Eng. Chem. Anal. Ed.*, 1944, **15**, 111). The empirical formula has been found to be PdR_2. This has been verified conductometrically. The chelate structure may be represented as :



The dissociation constant, and hence, the stability constant, the free energy of formation of the palladium complex and molecular extinction coefficient have been determined.

Experimental

3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine was prepared by the method given by Sogani and Bhattacharyya (*loc. cit.*). The reagent solution used for spectrophotometric work was $M \times 10^{-4}$ and for conductometric work, $M \times 10^{-3}$ solution.

Standard palladium chloride solution was prepared by dissolving approximately 0.5 g. of analytically pure palladium chloride in a small amount of HCl (dil.)

and making up the volume to 500 c.c. The palladium content of this solution was determined by precipitating it with dimethylglyoxime. It was further diluted to give $M \times 10^{-3}$ for conductometric measurements and $M \times 10^{-4}$ for spectrophotometric work.

10% HCl (v/v) and 10% sodium acetate (w/v) were used for adjusting the p_H of the solutions between 3.0 and 3.2 in the spectrophotometric work.

All absorption measurements were made with a Bausch & Lomb 'Spectronic -20' colorimeter, using 1 cm cuvette. A Beckman glass electrode p_H-meter (model H-2) was used for all p_H measurements. For conductivity measurements, a Kohlrausch Universal bridge was used. An 'Advance' A. F. generator (model H-1) was used as a source of alternating current.

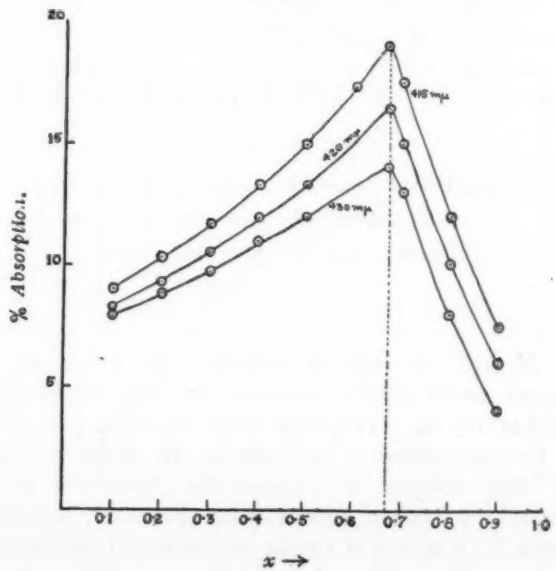
Nature of the Complex formed.—In a set of experiments, mixtures containing varying proportions of palladium : reagent (*i.e.* 1 : 1, 1 : 2, 1 : 3 etc.) were prepared and the optical densities at different wave-lengths in each case measured. In all the cases, the maximum absorption occurred at 415 mμ, thus indicating formation of only one complex with the reagent (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437).

Composition of the Complex

The molar composition of the palladium complex was investigated by the following methods.

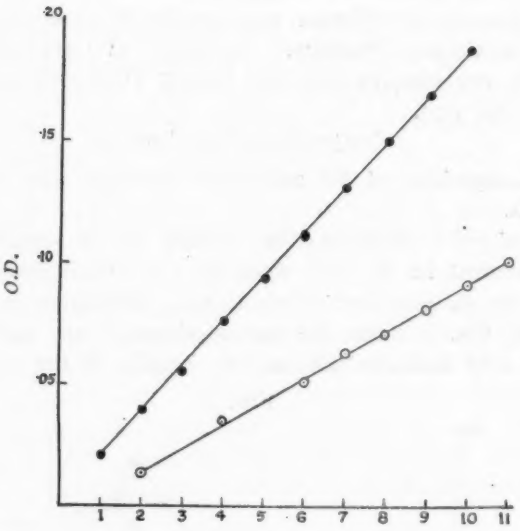
Job's Method.—For studying the formula of the complex by this method, the palladium content in the final solutions was varied between 2×10^{-6} *M* and 18×10^{-6}*M* and the p_H was kept at about 3.0. Absorption was measured at 415, 425 and 430mμ. Fig. 1 shows the curves obtained by applying this method. The maxima at 0.67 indicate PdR_2 as the formula of the complex.

FIG. 1



Slope Ratio Method.—The concentration of the variable component was varied from $1 \times 10^{-3} M$ to $10 \times 10^{-5} M$ in presence of excess concentration of $8 \times 10^{-4} M$ of the constant component. The p_H of the solution was kept at about 3.0. Fig. 2 records the measured optical density at 425 mμ, plotted against the concentration of the variable component. The slopes of the two straight lines give palladium to reagent ratio as 1:2, which is quite in confirmity with the previous method.

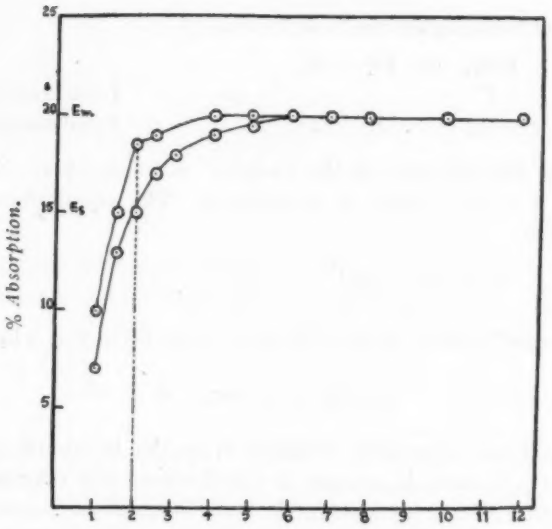
FIG. 2



Upper curve showing Pd varying and the lower one, the reagent varying. Conc. of the const. component = $8 \times 10^{-4} M$. p_H = 2.8-3. 425mμ.

Molar Ratio Method.—A series of solutions, in which the molar ratio of palladium to reagent varied from 1 : 0.5 to 1 : 10, was prepared and their absorption was measured at 425 mμ. The lower curve (a) in Fig. 3 does not show any sharp break owing to the dissociation of the complex in dilute solutions. By adding 5 c.c. of $M \times 10^{-3}$-KCl solution to suppress the dissociation of the complex, a method recommended by Harvey and Manning (*loc. cit.*), a sharp break is obtained (Fig. 3, upper curve 'b') at a ratio of 2 moles of reagent to 1 mole of palladium.

Fig. 3

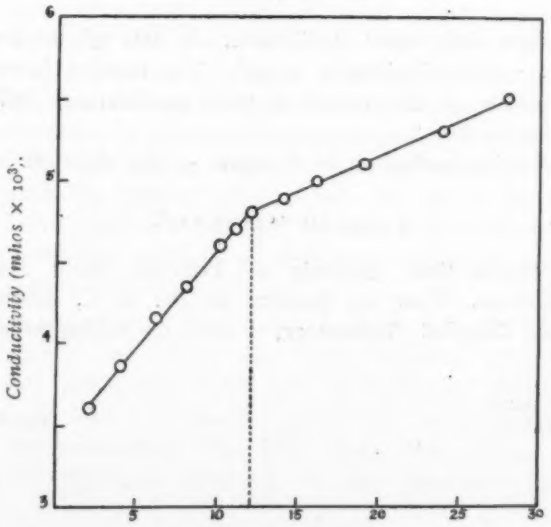


Moles reagent/mole Pd.

Pd conc. = $6\times10^{-6}M$ p_H=3—3.1. 425mμ.

Conductivity Method.—$M\times10^{-3}$-Palladium chloride (6 c.c.) solution was taken in a conductivity cell and its conductivity was measured. Equimolecular reagent solution was added from a burette. The observed conductivity was corrected for volume. Fig. 4 shows the conductivity values plotted against c.c. of the reagent added. The break in the curve at 12 c.c. of the reagent solution indicates PdR_2 as the formula of the complex. This is in agreement with the spectrophotometric results.

FIG. 4



$M\times10^{-3}$-*Reagent added (c.c.).*

DISCUSSION

The dissociation of the complex can be written as:

$$PdR_2 \rightleftharpoons Pd + 2R$$

C			...	Initial concentration
$C(1-\alpha)$	αC	$2\alpha C$	...	Final concentrations

where C is the total concentration of the complex in moles per, litre assuming no dissociation and α is the degree of dissociation. The equilibrium constant K is given by the equation:

$$K = \frac{\alpha C \times (2\alpha C)^2}{C(1-\alpha)} = \frac{4\alpha^3 C^2}{1-\alpha}.$$

The value of α may be obtained from the upper curve (a) in Fig. 3 by the following relationship

$$\alpha = (E_m - E_s)/E_m$$

where E_m is the maximum absorption obtained from the horizontal portion of the curve, when all the palladium is present in the form of the complex and E_s is the observed absorption of the stoichiometric molar ratio of the reagent to palladium in the complex. The value of α at room temperature (25°) on calculation comes to 0.25. The concentration 'C' of the complex is the same as the total concentration of palladium, which is $6 \times 10^{-6} M$. The value of K at 25° is equal to 3×10^{-12}. The stability constant K' of the complex is the reciprocal of the dissociation constant and is equal to 3.33×10^{11}.

The standard free energy of formation of the complex from palladium chloride and 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine is calculated from the relation,

$$\Delta F^\circ = RT \ln K,$$

where the terms have their usual significance. In this system the value of ΔF° works out to be -15.72 Kcal./mole at 25°. The reaction is accompanied with a considerable descrease of free energy at room temperature, indicating the spontaneous nature of the reaction.

Molecular extinction coefficient (ε) is equal to the slope of straight line 'a' in Fig. 2.

$$\varepsilon = \text{slope (a)} = 18\,75 \times 10^3.$$

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S-SUBSTITUTED THIOUREAS AS ANALYTICAL REAGENTS. PART III. S-METHYLTHIOUREA SULPHATE AS A COLORIMETRIC REAGENT FOR NICKEL AND COBALT

By S. K. Siddhanta and S. N. Banerjee

S-Methylthiourea sulphate has been employed as a colorimetric reagent for cobalt and nickel in ammoniacal medium The colour formed is deep enough to make the reagent sensitive. Beer's law is obeyed. The effects of variation of the ageing period, the p_H of the medium and the amount of the reagent have been studied, and suitable filters, indicated.

Applications of substituted thioureas in chemical analysis are few, and the only studies in this line appear to be those of Steiger (*Microchem.*, 1934-35, **16**, 193) and of Yoe and Overholser (*Ind. Eng. Chem. Anal. Ed.*, 1942, **14**, 435). These studies are mainly qualitative and limited to the determination of sensitiveness of colour reactions of a large number of substituted thioureas with many metallic ions. Siddhanta and Kundu (Part I, this *Journal*, 1955, **32**, 655) have found that nickel and copper can be estimated gravimetrically as their mercaptides by precipitating the latter from their alkaline solutions with *S*-methylthiourea sulphate. In Part II, Siddhanta and Banerjee (*ibid.*, 1958, **35**, 53) have successfully employed the same reagent for gravimetric estimation of silver. In the present work it has been found that cobalt also forms precipitate of deep brown cobalt methylmercaptide by adding a solution of *S*-methylthiourea sulphate to a hot alkaline solution of cobalt salt. The precipitate, however, reaches stoichiometric composition, $Co(CH_3S)_2$, only when the reagent added is less than the required amount. But with an excess of the reagent, the cobalt mercaptide precipitate becomes contaminated with oily oxidation products of methylmercaptide, thus restricting its use as a gravimetric reagent for cobalt.

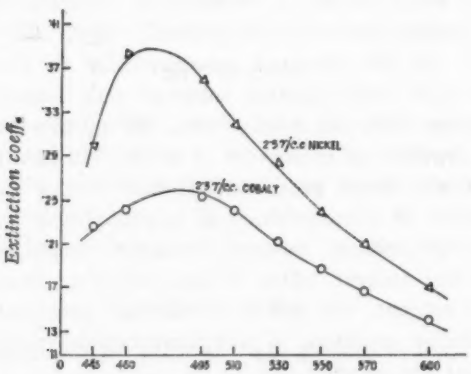
However, the reagent could form coloured stable colloidal solutions with very dilute solutions of nickel and cobalt salts. Such colloidal solutions obey Beer's law and, hence, both cobalt and nickel can be estimated colorimetrically. The estimations were made with a Duboscq colorimeter, using standard solutions of cobalt and nickel for comparison. The filter chosen was 495 mμ for cobalt and 495 mμ to 510 mμ for nickel, as indicated by the maximum optical density in

a Leifo photometer. The best result for cobalt was obtained with 180 times excess of the reagent, between p_H range 8.75 and 9.70, with cobalt concentration varying from 0.5 to 7.0 γ/c.c. and that for nickel with 40-fold excess of the reagent, between p_H range 9.14 and 9.51, with nickel concentration varying from 1.0 to 7.0 γ/c.c. The ageing period in case of cobalt is two hours, and that for nickel is one hour. The detection limit for cobalt is 0.1γ/c.c. and that for nickel is 0.45 γ/c.c.

EXPERIMENTAL

Cobalt methylmercaptide appears not to have been described in earlier literature. It is prepared as a brown precipitate by mixing solutions of cobalt nitrate and *S*-methylthiourea sulphate (molar ratio, 1 : 2) in ammoniacal medium at about 60°. [Found : Co(as sulphate), 38.63 ; S(as sulphate by peroxide fusion), 41.04. Calc. for $Co(CH_3S)_2$: Co, 38.55 ; S, 41.84%). Nickel methylmercaptide, $Ni(CH_3S)_2$ has been prepared by Siddhanta and Kundu (*loc. cit.*). Stock solutions of cobalt and nickel were prepared with cobalt nitrate (B.D.H.-AnalaR, Ni, 0.01%) and nickel sulphate (Hopkin and Williams Ltd., AnalaR, Co, 0.0005%) and estimated by the usual procedure. *S*-Methylthiourea sulphate (B.D.H., Lab. Reagent) solution, once prepared, could be kept for a few days without decomposition. All dilutions were made with bidistilled water on each day of the experiment from respective stock solutions. The p_H determinations were made with a Beckman p_H-meter (model H-2).

FIG. 1



Values of the extinction coefficient for nickel and cobalt solutions observed with different filters are represented in Fig. 1. The optimum time for keeping the solution mixtures before colorimetric comparison was determined from the horizontal portion of the plot of extinction coefficient against time, using different dilutions of cobalt (5.0, 2.5 and 0.5γ/c.c.) and nickel (7.5γ, 1.0γ/c.c.) solutions (vide Fig. 2).

TABLE I

Verification of Beer's law.

	1st. Soln.	2nd. Soln.
Reagent soln.	(*i*) 7 c.c. (0.0284 g. c.c.).	(*ii*) 2 c.c. (0.01422 g. c.c.).
Ammonia soln.	(*i*) 3 c.c. of 0.151 *N*.	(*ii*) 3 c.c. of 0.1409 *N*
Total volume	(*i*) 20 c.c.	(*ii*) 20 c.c.
Ageing period	(*i*) 2 hours.	(*ii*) 1 hour.

Cobalt solution (0.001%)					Cobalt solution (0.001%)				
1st. soln.		2nd. soln.			1st. soln.		2nd. soln.		
Vol.	Length.	Vol.	Length.	% Diff.	Vol.	Length.	Vol.	Length.	% Diff.
*10 c.c.	12.0 mm	3 c.c.	39.98 mm	0.05	13 c.c.	24.83 mm	8 c.c.	40 mm	0.9
9	15.2	3	45.0	1.4	12	20.66	8	30	3.3
*6	20.0	3	40.2	0.5	3	30.2	*2	45	0.7
7	19.2	3	45	0.5	8	22.7	6	30	1.0
4	20.1	2	40	0.5	10	24.0	8	30	0.0
9	22.3	5	40	0.5	9	25.0	7	32	0.4
14	20.3	8	35	1.5	9	25.0	*8	28.6	1.6
	Cobalt soln. (0.001%).					Nickel soln. (0.001%).			
3	41.4	5	25	0.75	14	10	4	35.30	0.80
4	39.2	8	20	2.00	4	20	2	40.63	1.57
1	40.0	*2	20.2	1.00	8	20	4	40 18	0.48
4	38.9	10	16	2.75	10	18	6	30.00	0.00
2	45.2	6	15	0.40	15	40	14	39.02	9.80
1	39.3	0.8	40	18.20	6	30	8	22.44	0.25
0.8	18 2	0.4	40	9.00	10	35	15	24.20	3.72
					6	40	12	20.10	0.48

* Solutions having an ageing period of six hours.

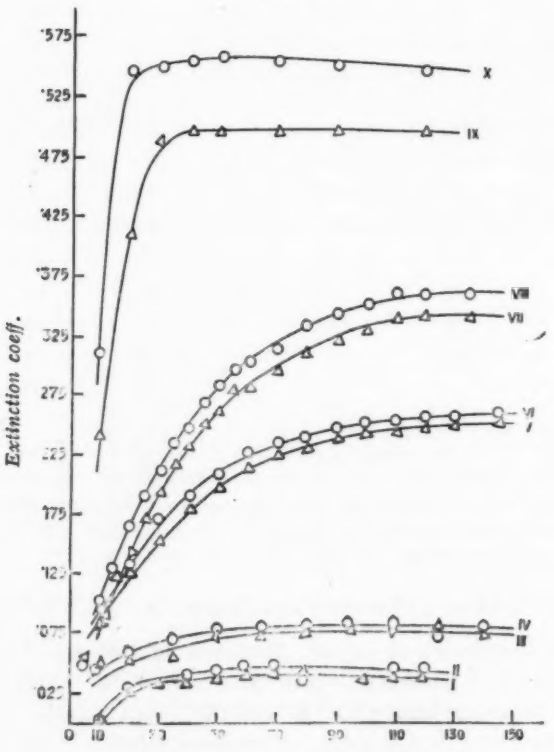
N.B. It has been observed in the case of cobalt that if the solution in one limb is exposed to air during the ageing period, while that in the other limb is not exposed, the readings differ by a large amount. If, now, the unexposed solution is exposed for some time to air and the readings are again taken, then the error comes within the usual limit. So there is some relation between intensity of colour formation and exposure to air in this case.

Effect of Variation of Ammonia and Reagent in Cobalt Estimation

The results of comparison of colour, developed in two solutions side by side, as done in a Duboscq colorimeter, have been shown in Table II. The first solution contained in every case 5 c.c. of 0.001% cobalt solution, 2 c.c. of the reagent solution (0.01422 g./c.c.), 3 c.c. of ammonia solution (0.151 *N*) and sufficient water to make the total volume 20 c.c., giving a p_H value of 9.12 (a p_H at which Beer's law is obeyed). The second solution contained in every case, 5 c.c. of the same cobalt solution, 2 c.c. of the same reagent solution, varying volumes of ammonia and enough water to make the total volume 20 c.c., for studying the effect of the variation of ammonia (top left of Table II, columns 1,2 and 3; the

lengths of the second solution required to match 30 mm of the first solutions have been shown in column 3). In order to study the effect of reagent variation, both the solutions always contained 5 c.c. of cobalt solutions (0.001%), varying volumes of the reagent and 3 c.c. of 0.151*N* ammonia solution, whereby p_H values varied from 8.95 to 9.20 for the 'first' solution and from 8.95 to 9.32 for the 'second' solutions. The results have been shown in columns 4, 5 and 6 (top right, Table II). The effect of simultaneous variation of cobalt and the reagent has been shown in columns 4, 5 and 6 (bottom right, Table II). In this case also, both the first and second solutions were made up to 20 c c. after mixing up the cobalt, reagent and ammonia solutions. In each case an ageing period of 2½ to 3 hours was allowed before the comparison of colour was made.

FIG. 2



I: 510 mμ, 1.0 γ/c.c. Ni.
II: 495 „ „ „
III: 510 „ 0.5 „ Co.
IV: 495 „ „ „ „
V: 510 „ 2.5 „ „
VI: 495mμ, 2.5 γ/c.c. Cc.
VII: 510 „ 5.0 „ „
VIII: 495 „ 5.0 „ „
IX: 510 „ 7.5 „ Ni.
X: 495 „ „ „ „

TABLE II

Cobalt soln. = 5 c.c. of .001%. Total vol. = 20 c.c. Ageing time = 2½ to 3 hours.

Vol. of NH_4OH (0.151N) in 2nd. soln.	p_H (2nd. soln.)	Length (2nd. soln. against 30 mm of 1st. soln.).	Vol. of reagent soln. (0.01422 g./c.c.) in 1st. soln.	2nd. soln.	Length (2nd. soln., against 30 mm. of 1st. soln.).
Variation of ammonia.			Variation of reagent.		
0.5 c.c.	8.60	32.88 mm	2.0 c.c.	1.0 c.c.	40.50 mm
1.0	8.75	29.80	4.0	2.5	32.50
1.5	8.87	30.10	3.0	2.0	34.07
2.0	9.00	29.83	3.5	2.5	32.45
4.0	9.21	30.66	2.0	1.5	35.37
6.0	9.35	30.32	4.0	3.0	30.23
7.0	9.42	29.50	3.0	3.5	29.70
8.0	9.53	29.77	3.0	4.0	29.30
10.0	9.68	30.33	Simultaneous variation of cobalt and reagent.		
12.0	9.69	29.80	*6	7	*30.1
13.0	9.72	31.13	*6	8	*29.7
			≠6	7	≠29.9
			≠6	8	≠29.2
Signs * and ≠ correspond to 4 c.c. of 0.001%			*6	6	≠15.3
and 8 c.c. of 0.001% cobalt solns. respectively.			*7	7	≠15.1
In these cases other conditions are : ammonia			*8	8	≠15.2
solution, 3 c.c. of 0.151 N; ageing time, 2 hours;			*6	7	≠15.4
reagent conc., 0.0284 g./c.c., and total volume,			*7	8	≠15.0
20 c.c.			*6	8	≠14.5

It may be observed from the above table, that for cobalt estimation the reaction is incomplete below p_H 8.75. There is, however, a tendency for the precipitate to coagulate above p_H 9.70. The minimum reagent to be added in the estimation of cobalt is about 180 times the amount theoretically required.

Effect of Variation of Ammonia and Reagent in Nickel Estimation

From Table III it is observed that the optimum p_H range for nickel estimation is between 9.14 and 9.51 and the minimum amount of the reagent to be used is 40 times the theoretically required value.

TABLE III

Ni soln. = 10 c.c. of 0.001%. Total vol. = 20 c.c. Ageing time = ½ hour.
(Length of first solution for matching = 30 mm).

First solution. Volume added of		p_H.	Second solution. Volume added of		Length (against 30 mm. of 1st. soln.).	p_H.
Ammonia (0.1409N).	Reagent soln. (0.01422 g./c.c.).		Ammonia (0.1409N).	Reagent soln. (0.01422 g./c.c.).		
			Variation of ammonia			
3 c.c.	2 c.c.	9.30	1 c.c.	2 c.c.	No. match possible.	8.99
3	,,	9.30	2	,,	29 13 mm.	9.14
4	,,	9.45	3	,,	30.10	9.30
4	,,	9.45	4	,,	30.17	9 45
3	,,	9.30	3	,,	29.62	9.30
2	,,	9.15	2	,,	29.80	9.14
			Variation of the reagent.			
3	2.6	9.25	3	2.6	30.18	9.20
,,	2.0	9.39	,,	2.0	29.95	9.35
,,	1.3	9.47	,,	1.3	30.21	9 51
,,	0.7	9.75	,,	0.7	25.00	9.72
,,	2.0	9.35	,,	2.6	30.72	9.20
,,	1.3	9.51	,,	2.0	29.91	9.35
,,	0.7	9.72	,,	1.3	28.00	9.51
,,	1.3	9.51	,,	2.6	29.59	9.20

Mixtures of reagent solution, ammonia and either nickel or cobalt solution have been compared against blank solutions containing the reagent and ammonia under identical conditions in the Duboscq colorimeter, and the minimum concentration of the metal, below which the colour difference becomes imperceptible, has been found out.

The authors wish to thank Prof. S. K. Bhattacharyya, Head of the Department of Applied Chemistry, for facilities provided during this work.

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APPLICATION OF REFRACTIVE INDEX IN THE STUDY OF CHEMICAL CONSTITUTION. PART II. DETERMINATION OF TRANSITION POINT OF CERTAIN HYDRATED INORGANIC SALTS IN SOLUTION BY REFRACTIVE INDEX

By Shiam Sunder Joshi and D. P. Joshi

Refractive index values of aqueous solutions of sodium sulphate and zinc sulphate between 20° and 50° show abrupt changes at certain temperatures. The values, so obtained, nearly agree with their transition points, determined by other methods.

Variations in the values of refractive index are usually uniform with rise of temperature. But it was observed by us earlier (this *Journal*, 1956, **33**, 149) that in the case of aqueous solutions of sodium carbonate and magnesium sulphate, there were abrupt changes at certain temperatures. These were found nearly the same as the transition points, determined by other methods. The work has now been extended to sodium sulphate and zinc sulphate, and in these cases also similar phenomenon has been noticed.

For these studies aqueous solutions of the salts of four different concentrations have been used. In the case of sodium sulphate, the concentrations of the solutions employed were $M/2$, $M/10$, $M/50$ and $M/250$ and the refractive index determinations were made between 20° and 50°. With all the four solutions, an irregularity in the uniform variation of refractive index was observed at 32.4°. This is in agreement with the values of previous workers by other methods: 32.6° (Dunstan and Langton, *J. Chem. Soc.*, 1912, **101**, 418), 32.4° (Rechards and Wells, *Z. physikal. Chem.*, 1903, **43**, 471), 32.4° (Wuite, *ibid.*, 1914, **86**, 349), 32.55° (Hartshorne, *J. Chem. Soc.*, 1924, 2096). Another temperature of abrupt refractive index

Fig. 1

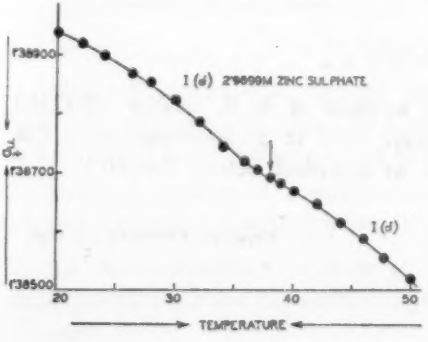
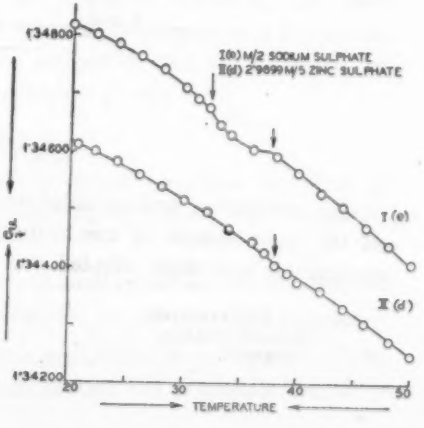


Fig. 2

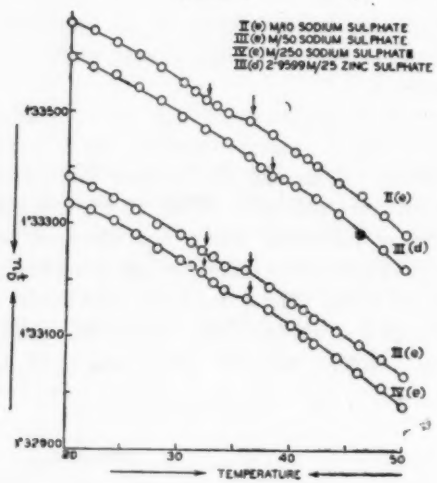


variation has also been observed in case of all the solutions, but the value is not the same in all cases. This temperature was found to be 37.6° in case of the most concentrated solution ($M/2$) and 36.6° in the other three cases. [vide curve I(e), Fig. 2 ; II(e), III(e) and IV(e), Fig. 3]. This transition point has not been observed by previous workers, using other methods.

In the literature, another transition point (24.4°, Wuite ; *loc. cit.* ; 23 465° ±.004, Washburn and Clem, *J. Amer. Chem. Soc.*, 1938, **60**, 754) has been reported. This was not observed by us.

With four aqueous zinc sulphate solutions (2.9899M, 2.9899$M/5$, 2.9899$M/25$ and 2.9899$M/125$), the abnormal changes in the variation of refractive index within 20°-50° have been observed to take place in all cases only at 38° [vide curves-I(d), Fig. 1 ; II(d), Fig. 2 ; III(d), Fig. 3.] In the literature also within the range 20°-50°, only one transition temperature appears to have been mentioned at 37.9° (Cohen and Hilterschij, *Z. physikal. Chem.*, 1925, **115**, 440, 443).

FIG. 3



EXPERIMENTAL

The crystalline sodium sulphate and zinc sulphate of A. R. quality (B.D.H.) and the same sample of conductivity water were used in all determiuations. The experimental procedure adopted was the same as described before (*loc. cit.*).

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STUDIES IN COMPLEX FORMATION WITH COLLOIDAL MERCURISULPHOSALICYLATE. PART III. COMPLEX URANYL MERCURISULPHOSALICYLATE

By Rajendra S. Singh and Satya Prakash

Potentiometric, conductometric and colorimetric studies of the complex formation between uranyl nitrate and potassium chloromercurisulphosalicylate show that only one complex containing the reactants in the ratio of 1 : 1 is formed at p_H 4.5. During the complex formation, the phenolic hydrogen is displaced and the co-ordination takes place between the oxygen atoms of phenolic and carboxyl groups.

In Parts I and II (Singh and Prakash, this *Journal*, 1957, **34**, 197, 807) the studies of complex formation of mercurisulphosalicylate with beryllium and aluminium have been reported. Physico-chemical studies on the formation of uranyl mercurisulphosalicylate complex in solution have been reported herein.

Sulphosalicylic acid forms a solid compound corresponding to the composition $(C_6H_3-OH-SO_3-COO)_2U$ with uranium (St. Weil and St. Rozenblum, *Bull. Trans. Inst. Pharm.*, Poland, 1902, **1**, 1). Wienland and Häger (*Z. anorg. Chem.*, 1927, **180**, 193) prepared a large number of complex compounds of uranyl ion with salicylic acid. Uranyl complexes with citric, lactic, malic and tartaric acids have been investigated by Feldman *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 2315, 3593; 1954, **76**, 2114). Anderson *et al.* (*ibid.*, 1949, **71**, 909) have investigated the complex formation of uranyl ion with sulphosalicylic acid spectrophotometrically. They have shown that a mixture containing the reactants has a maximum absorption at a p_H range of 4.00 – 4.70 at 444mμ. Using Job's method (*Ann. chim.*, 1928, *x*, **9**, 113) of continued variation, they have found that only one complex containing uranyl and sulphosalicylic acid in the ratio of 1 : 1 is formed. No definite structure has been suggested, but the co-ordination has been assumed to be between the carboxyl and sulphonic groups.

Experimental

Standard solutions of uranyl nitrate were prepared by direct weighing of Baker's analysed sample of $UO_2(NO_3)_2$, $6H_2O$ and dissolving in water. Fresh solutions were employed to avoid effects due to hydrolysis.

Standard solutions of potassium chloromercurisulphosalicylate and its monosodium salt were prepared as described earlier (Singh and Prakash, *loc. cit.*, p. 197).

All measurements were made at a constant temperature of 32° ± 0.1°. The specific conductivity and p_H measurements were made as described previously (*loc. cit*).

The colorimetric measurements were made with a Klett-Sommerson photoelectric colorimeter, using Klett filters Ks 47(445 – 505 mμ) and Ks 54 (520 – 580 mμ).

The procedure adopted here was the same as described previously (*loc. cit.*). The mixture solutions with varying amounts of alkali were allowed to stand for 24 hours when precipitation occurred as a result of the attainment of equilibrium.

According to Job's method (*loc. cit.*), different volumes of uranyl and potassium chloromercurisulphosalicylate were mixed in various ratios (0.1 – 1.0) of the concentration of uranyl ion to the total concentration of uranyl ion and potassium chloromercurisulphosalicylate. The p_H of the mixture solution was kept constant at 4.50 by the addition of alkali, keeping the total volume constant.

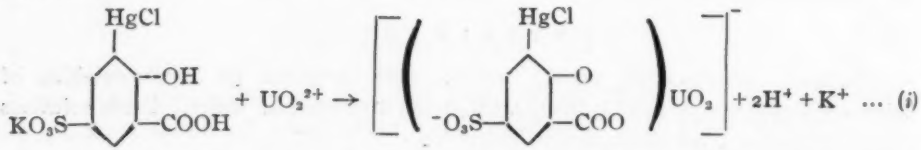
For the colorimetric measurements, turbid solutions were centrifuged to obtain clear solutions.

DISCUSSION

Fig. 1 represents the changes in the p_H when uranyl nitrate and potassium chloromercurisulphosalicylate, in different proportions, were titrated with alkali respectively. The '*a*' values, plotted as abscissa are the number of equivalents of alkali added per mole of uranyl ion. Curves A, B, C and D are for $6.25 \times 10^{-3} M$ solutions in (*i*) uranyl nitrate (A), (*ii*) 1 : 1 and 1 : 2 mixtures of uranyl nitrate and potassium chloromercurisulphosalicylate (B and C) and (*iii*) 1 : 1 mixture of uranyl nitrate and monosodium potassium chloromercurisulphosalicylate (D). Curves E and F are for $6.25 \times 10^{-3} M$ solutions of mercurisulphosalicylic acid and potassium chloromercurisulphosalicylate. When alkali is added to uranyl nitrate (A), no precipitation occurs until nearly two equivalents of alkali have been added (p_H 4.60).

The neutralisation of mercurisulphosalicylic acid (E) and its potassium chloride salt (F) has been discussed in an earlier communication (Singh and Prakash, *loc. cit.*, p. 197).

When one equivalent of potassium chloromercurisulphosalicylate is added to uranyl nitrate (B), the initial p_H (2.40) is slightly lower than that of potassium chloromercurisulphosalicylate (2.60) or uranyl nitrate (3.32) alone. The mixture solution is orange-red in colour which deepens on the addition of alkali. The curve shows an inflection at $a = 2$, indicating the formation of a complex. Turbid solutions were obtained at p_H 7.0 and above with precipitation of uranyl hydroxide (at p_H 7.60). The reaction may be represented by



When two equivalents of potassium chloromercurisulphosalicylate are added to uranyl nitrate (C), an inflection occurs at $a = 3$, indicating that only one complex with 1 : 1 ratio is formed. No turbid solutions were obtained in this case and the precipitation occurred at p_H 9.20. The presence of an excess of potassium chloromercurisulphosalicylate thus appears to increase the stability of the complex formed.

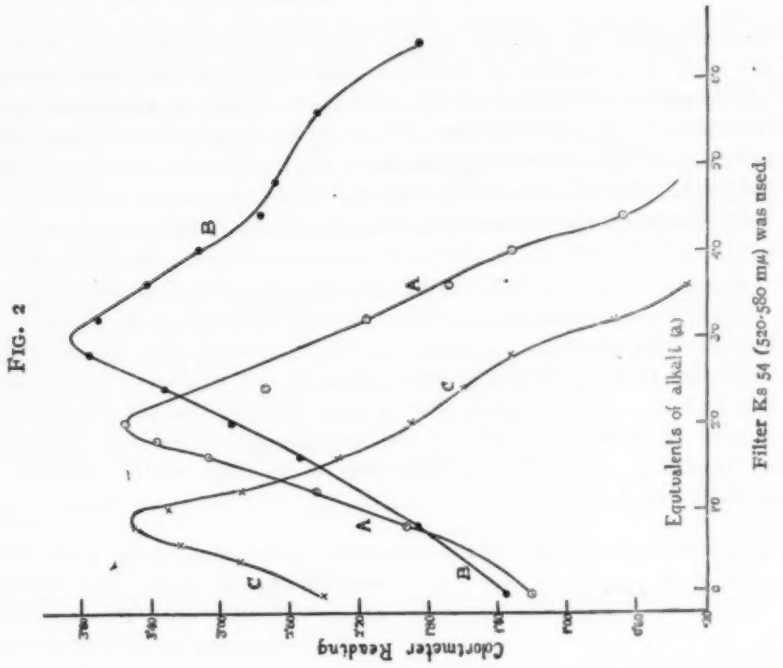


FIG. 2

Filter Ks 54 (520-580 mμ) was used.

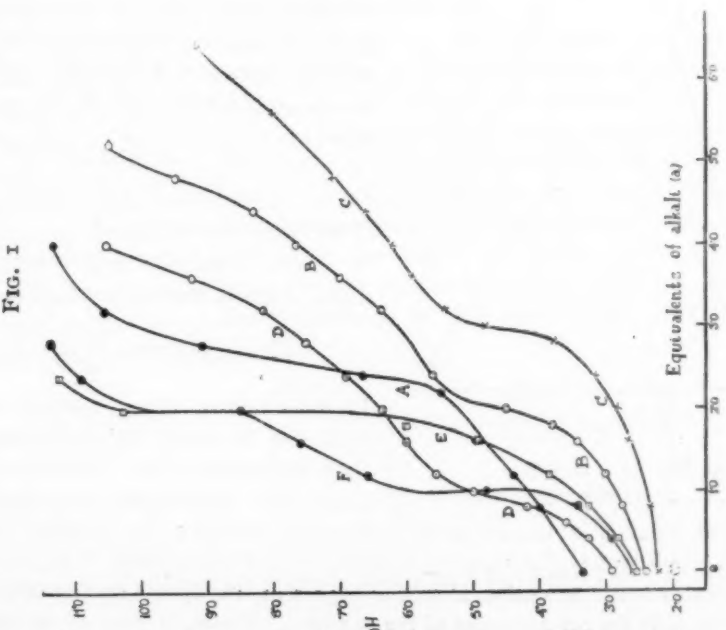
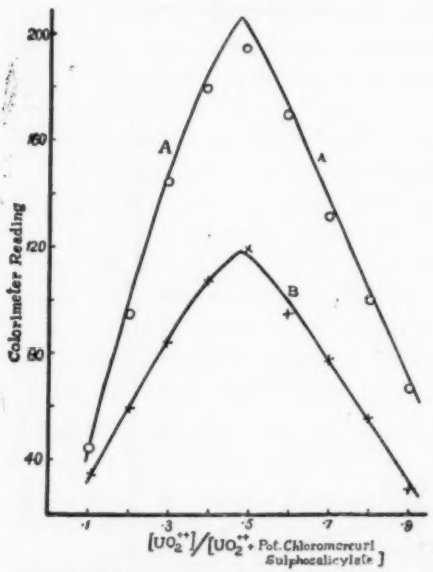


FIG. 1

Fig. 2 represents the changes in the colorimeter readings when $6.25 \times 10^{-3}M$ solutions of (*i*) 1 : 1 mixture of uranyl nitrate with potassium chloromercurisuiphosalicylate (A) and its monosodium salt (C), and (*ii*) 1 : 2 mixture of uranyl nitrate and potassium chloromercurisulphosalicylate (B) are titrated with alkali respectively. The abscissa represents the number of equivalents of alkali added (*a*). Curves A and C show a continuous rise with the addition of alkali, reaching a maximum value at $a = 2$ and $a = 1$ respectively, after which the values decrease rapidly. The maximum colorimeter reading is same in both the mixtures, as the same complex is formed. Curve B also shows a maximum at $a = 3$, but the value is greater than that obtained with 1 : 1 mixtures (A and C). Basing on the observation of Anderson *et al.* (*loc. cit.*) that the uranyl sulphosalicylate complex exists in a partly dissociated state, the higher maximum value with the 1 : 2 mixture may be ascribed to the decreased dissociation of the complex formed. The maxima offer a clear evidence for the formation of only one complex of ratio 1 : 1, and for the displacement of phenolic hydrogen during complex formation. All the maxima occur at p_H 4.50, which indicates that the complex is formed at that p_H.

Fig. 3 represents the study of the composition of the complex by Job's method at a constant p_H of 4.50. The concentrations of the solutions were $2.00 \times 10^{-3}M$. The abscissa represents the ratio of the concentration of uranyl ion to the total concentration of uranyl ion and potassium chloromercurisulphosalicylate, *i.e.*, $[UO_2^{2+}]/[UO_2^{2+}]$ + [pot. chloromercurisulphosalicylate]. Consider the formation of a complex AB_n, where A is a metallic ion and B, a complexing agent :

FIG. 3



A—with filter Ks 47 (445-505 mμ).
B— „ „ Ks 54 (520-580 mμ).

$$A + nB \rightleftharpoons AB_n$$

$$K = [AB_n]/[A] \times [B]^n.$$

If we impose the restriction

$$[A] + [B] = C \text{ (constant)},$$

it can be shown that when AB_n is maximum

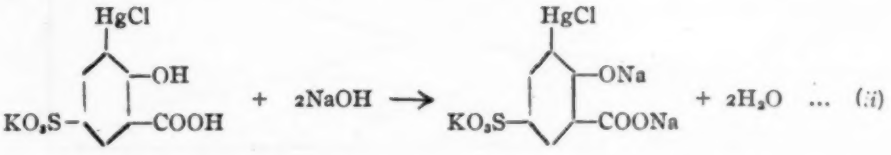
$$[B]/[A] = n \text{ or } \frac{d(AB_n)}{d(A)} = 0.$$

In other words, for a constant total concentration of metal and complexing agent, the concentration of the complex is greatest when the metal and complexing agent are brought together in the ratios in which they exist in the complex (Martel and Calvin, "Chemistry of Metal Chelate Compounds", Prentice Hall, N.Y., p. 29, 1953). If the complex is the only coloured substance present, the optical density of the solution is proportional to the concentration of the complex. Hence, a plot of optical density

and composition of solution under the restriction imposed would give a curve with a maximum at the composition corresponding to the formula of the complex.

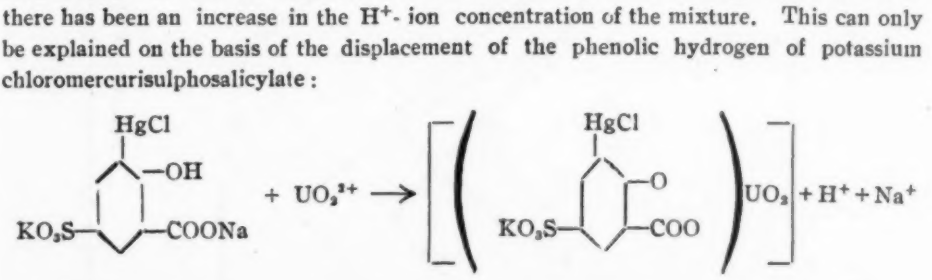
In our experiments, though the uranyl nitrate was slightly coloured, it did not affect the colorimeter readings of the complex. From the graph it can be seen that, at a constant p_H of 4.50, the maximum occurs at 0.5 mole ratio of the concentration of uranyl ion to the total concentration of uranyl ion and potassium chloromercurisulphosalicylate, which indicates the formation of a complex in which the molar ratio of metal ion to complexing agent is 1 : 1.

Fig. 4 represents the changes in the specific conductivity when $6.25 \times 10^{-3}M$ solutions in (*i*) uranyl nitrate (A), (*ii*) 1 : 1 mixture of uranyl nitrate with potassium chloromercurisulphosalicylate (B) and (*iii*) potassium chloromercurisulphosalicylate (D) were titrated with alkali respectively. The abscissa represents the equivalents of alkali added (*a*). D shows a minimum at $a = 1$, and a break at $a = 2$, which can be explained by the following equation :



The 1 : 1 mixtures of uranyl nitrate with potassium chloromercurisulphosalicylate (B) show minima at $a = 2$ and $a = 1$ respectively, which indicates the displacement of the phenolic hydrogen during the complex formation.

Fig. 5 represents the changes in the p_H and colorimeter readings with the progressive addition of uranyl nitrate to monosodium salt of potassium chloromercurisulphosalicylate. The concentration of both the solutions were $6.25 \times 10^{-3}M$. A represents the p_H of the mixture, while A′ is for uranyl nitrate alone at similar concentrations. B is the colorimeter reading for the mixture solution. With the addition of uranyl nitrate, the p_H of the monosodium salt (6.25) decreases rapidly and comes to nearly a constant value when one equivalent of uranyl nitrate has been added. It will be seen that A lies below A′, which clearly indicates that there has been an increase in the H^+- ion concentration of the mixture. This can only be explained on the basis of the displacement of the phenolic hydrogen of potassium chloromercurisulphosalicylate :



This clearly shows that the phenolic hydrogen is displaced even in acidic medium (p_H 2.70).

FIG. 4

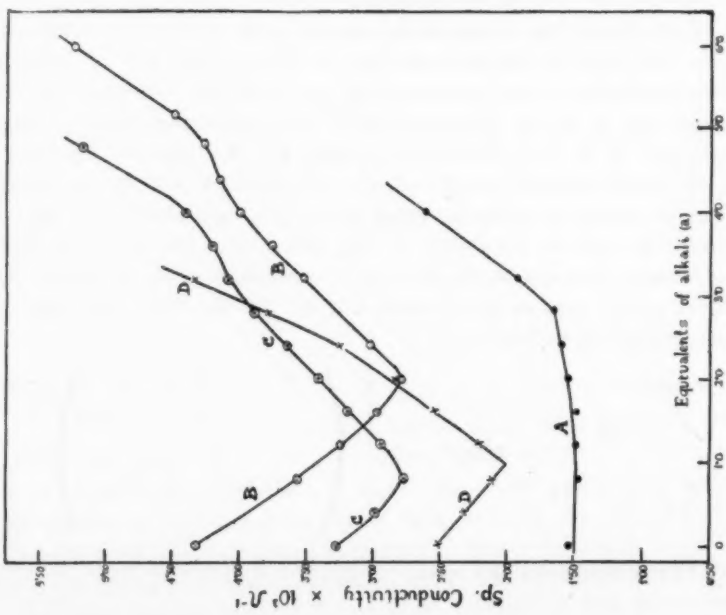
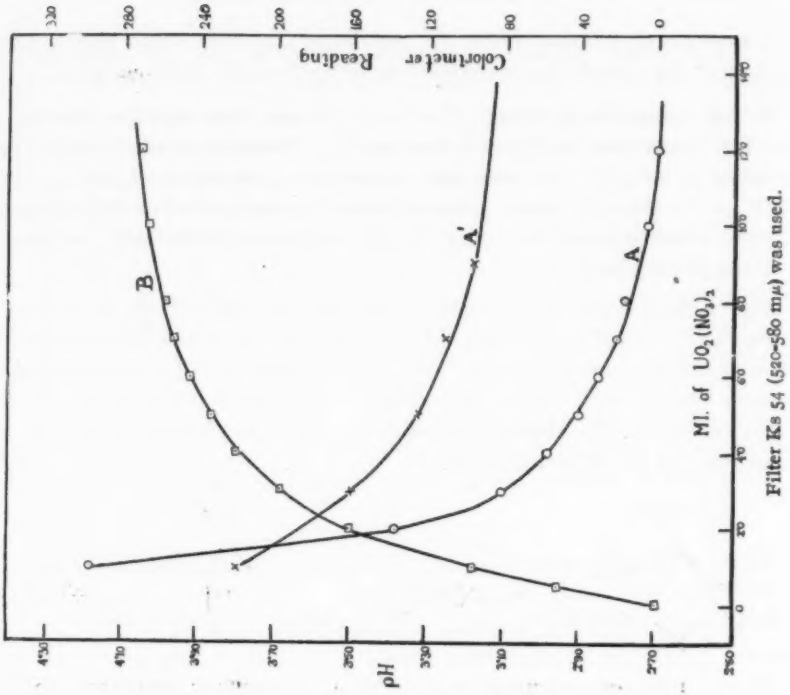


FIG. 5



Filter Ks 54 (520–580 mμ) was used.

The colorimeter reading curve (B) shows a gradual increase with the addition of uranyl nitrate and reaches almost a constant value when one equivalent has been added. It will be seen that with the addition of uranyl nitrate to monosodium potassium chloromercurisulphosalicylate, there is a decrease in the p_H value together with an increase in the colorimeter reading. This fact provides a more clear evidence that the phenolic hydrogen is displaced during complex formation. (Uranyl nitrate alone gives a negligible colorimeter reading.)

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2-MERCAPTO- AND 2-METHYL-BENZIMIDAZOLES AS REAGENTS FOR SILVER

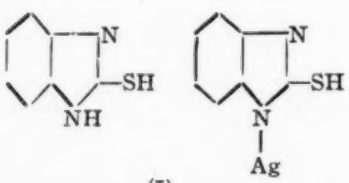
By R. L. Dutta

2-Mercapto- and 2-methyl-benzimidazoles have been found to be useful reagents for gravimetric estimation of silver in ammoniacal medium in the presence of other metals by masking them with appropriate reagents. The silver salts of these reagents are stable towards light, and heat, and determination can be made rapidly

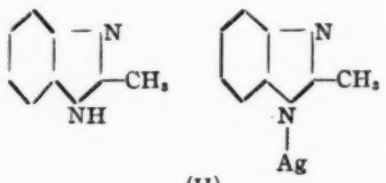
In an earlier communication (Dutta, this *Journal*, 1956, **33**, 389) the use of benzimidazole as a reagent for the gravimetric determination of silver was reported. In the present paper are recorded the results of a study with 2-mercapto- and 2-methylbenzimidazoles.

2-Mercaptobenzimidazole (I) was first studied by Kuras as a precipitating agent (*Chem. Abst.*, 1939, **33**, 941, 7233, 9200). He has described procedures for gravimetric estimation of copper, cadmium and lead, but has made only qualitative observations on the precipitation of silver, mercury and gold. This reagent has also been used for the detection and spectrophotometric estimation of palladium (Steigmann, *Chem. Abst.*, 1943, **37**, 3689 ; Xavier, *Proc. Ind. Sci. Congress*, 1956, Part III, p. 63).

Feigl and Gleich (*Monatsh.*, 1928, **49**, 385) have reported the silver salt of 2-methylbenzimidazole (II), but the reagent has not been utilised for the gravimetric estimation of silver.



(I)



(II)

These two substituted benzimidazoles precipitate silver quantitatively in ammoniacal medium and the precipitates being extremely granular, filtration becomes an easy proposition. The precipitates are insoluble in hot water, dilute ammonia but soluble in sodium thiosulphate and sodium cyanide. After drying at 120°, the silver salt of 2-methylbenzimidazole and of 2-mercaptobenzimidazole conform to the composition $C_8H_7N_2$ Ag and $C_7H_5N_2S$ Ag, and the gravimetric factors therefore become 0.4513 and 0.41961 respectively. The interfering effects due to copper, nickel, cobalt, manganese, zinc, cadmium, lead, bismuth and thallium have been eliminated by masking them with EDTA. But mercury interferes. Sodium potassium tartrate has been used to keep metals like aluminium, beryllium, uranium in solution. In presence of appreciable amounts of ammonium salts, 2-methylbenzimidazole gives slightly low values, whereas 2-mercaptobenzimidazole still gives quantitative values.

EXPERIMENTAL

2-Methylbenzimidazole was prepared according to Phillips (*J. Chem. Soc.*, 1928, 172). Van Allan and Deacon ("Org. Synthesis", **30**, p. 56) have described the preparation of 2-mercaptobenzimidazole. ** Preparation of silver nitrate solution and EDTA has been described in the earlier communication (Dutta, *loc. cit.*).

Effect of p_H on the Precipitation of Silver.—Precipitation in neutral or ammoniacal medium afforded a highly granular product. Precipitation in acid range resulted in a slimy product. In Table I some of the results showing the effect of p_H are described.

TABLE I

	With 2-mercaptobenzimidazole. Ag taken = 0.0473 g. (determined as chloride)				With 2-methylbenzimidazole. Ag taken = 0.0440 g.			
p_H (of the filtrate)	6.9	8.1	8.8	10.1	7.5	8.2	9.7	10.56
Ag found (in g.)	0.0474	0.0475	0.0474	0.0475	0.0439	0.0440	0.0440	0.04395

Procedure.—p_H of the silver nitrate solution was adjusted to within the range 8-10. The solution was warmed on the water bath, treated with an excess of the hot reagent solution with constant stirring and the mixture was then digested on the water-bath for 15-30 minutes. The precipitate formed was filtered through a Gooch crucible, washed with hot water, dried at 120° and weighed as $C_7H_5N_2SAg$ (for 2-mercaptobenzimidazole) or as $C_8H_7N_2Ag$ (for 2-methylbenzimidazole). Some of these results are recorded in Table II.

TABLE II

With 2-mercaptobenzimidazole.			With 2-methylbenzimidazole.		
Ag taken.	Ag salt.	Ag found.	Ag taken.	Ag salt.	Ag found.
0.09460 g.	0.2262 g.	0.0949 g.	0.0880 g.	0.1947 g.	0.0880 g.
0.07568	0.1800	0.0755	0.0704	0.1560	0.0701
0.04730	0.1130	0.04774	0.0440	0.09715	0.0438
0.02838	0.0679	0.02837	† 0.0440	0.09715	0.0438
0.00946	0.0225	0.00944	* 0.0440	0.09735	0.0440
* 0.04730	0.1130	0.04740			
† 0.04730	0.1130	0.04740			

† In presence of EDTA.
* In presence of NaK-tartrate.

Effect of Ammonium Salts.—The effect of ammonium salts on the precipitation of silver with these two reagents is shown in Table III.

TABLE III

With 2-methylbenzimidazole.			With 2-mercaptobenzimidazole.		
Ag taken.	Amm. salt added.	Ag found.	Ag taken.	Amm. salt added.	Ag found.
0.0880 g.	NH_4Cl 0.5 g.	0.0858 g.	0.0473 g.	NH_4NO_3 2 g.	0.0474 g.
	,, 1.0	0.0836		,, 5	0.04745
	NH_4NO_3 2.0	0.0882		NH_4Cl 1	0.04740
				2	0.04740

** 1% Solutions of 2-methyl- and 2-mercapto-benzimidazole were made in hot water and hot aq. alcohol respectively.

Determination of Silver in presence of Cu, Ni, Co, Mn, Pb, Zn, Cd, Bi, Hg, Tl *etc.*—To the silver solution having any of these interfering metals was added with stirring 20 c.c. of the ammoniacal EDTA solution ; the mixture was warmed on the water-bath and silver precipitated with excess of any of the reagents.

Determination in presence of Be, Al, U, Th *etc.*—To the slightly acid solution of silver and these metals was added sodium potassium tartrate (5 g.) and the mixture then treated with ammonia solution. If a precipitate of the hydroxide formed, some more tartrate was added and the mixture heated to get a clear solution. Afterwards silver was precipitated as usual.

In Table IV are recorded some typical results of estimation of silver in presence of some interfering ions.

TABLE IV

Ions.	Amount added.	* Ag found with 2 Mercapto-B	2-Methyl-B.	Ions.	Amount added.	* Ag found with 2-Mercapto-B.	2-Methyl-B.
Cu^{2+}	63 5 mg.	0.0474 g.	0.0440 g.	Pb^{2+}	207.2 mg	0 04735 g.	0.04387 g
Ni^{2+}	58.7	0.0474	0.04389	Tl^{+}	204.0	0.04745	0.04398
Co^{2+}	59.0	0.04745	0.04302	Bi^{3+}	209.0	0.04740	0.04410
Mn^{2+}	54.9	0.04745	...	Be^{2+}	36.0	0.04745	0.0440
Mg^{2+}	48.0	0.0473	...	Al^{3+}	52.0	0 04740	0.0441
Hg^{2+}	2000	Interferes	0.0440	Th^{4+}	232.0	0.04730	0.04415
Zn^{2+}	65.3	0.01745	...	UO_2^{2+}	135.0	0.04725	0.04410
Cd^{2+}	112.4	0.0474	0.0439				

Ag present in case with 2-mercapto B was 0.0473 g. and with 2-methyl-B was 0.044 g.
B denotes benzimidazole.

Composition of the Precipitates.—The dried silver salts were ignited to metallic silver, and nitrogen was determined by combustion.

(1) *Silver salt of 2-mercaptobenzimidazole* : (Found : Ag, 42.30 ; N, 11.12. $C_7H_5N_2S$ requires Ag, 41.96 ; N, 10.90 %).

(2) *Silver salt of 2-methylbenzimidazole* : (Found : Ag, 45.00 ; N, 11.61. $C_8H_7N_2$ Ag requires Ag, 45.13 ; N, 11.72 %).

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ON THE FORMATION OF COMPOUNDS IN ORGANIC SOLVENTS. PART II. FORMATION OF ALKALI AND ALKALINE EARTH METAL IODOMERCURIATES, ALKALI METAL IODOCADMIATES AND CADMIUM IODOMERCURIATES

By Sarju Prasad and Prabhoo Dayal Sharma

The formation of complex and double salts of HgI_2 and CdI_2 with univalent and bivalent metal iodides and also the interaction of HgI_2 and CdI_2 in organic solvents have been studied. The following compounds have been prepared and their properties studied: $NH_4I.HgI_2.C_2H_5OH$; $2NH_4I.CdI_2$; $NH_4I.CdI_2.C_2H_5OH$; $2LiI.HgI_2.6C_2H_5OH$; $NaI.HgI_2.2C_2H_5OH$; $NaI.HgI_2.2HOAc$; $NaI.HgI_2.2(CH_3)_2CO$; $KI.HgI_2.2C_2H_5OH$; $KI.HgI_2.2Py$; $MgI_2.HgI_2.8C_2H_5OH$; $2HgI_2.CaI_2$; $CaI_2.3HgI_2.6C_2H_5OH$; $2HgI_2.SrI_2$; $CdI_2.3HgI_2$; $HgI_2.2CdI_2$. 10 acetamide; CdI_2. 6 benzamide; $CdI_2.6Py$ and $HgI_2.2Py$.

The formation of complex and double salts of HgI_2 and CdI_2 with uni- and bivalent metal iodides and also the interaction of HgI_2 and CdI_2 in aqueous medium have been studied by several workers (cf. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1923, Vol. IV, pp. 582-84, 925-41). Hietnan and Siller (*Svensk. Kem. Tied.*, 1947, **59**, 228) studied the ternary system, HgI_2-CdI_2-H_2O at 50°, 75°, 100°, and found that tetragonal form of HgI_2 formed mixed crystals containing 0-50% CdI_2. Practically no work on the subject has been done in non-aqueous media, and the present investigation has therefore been undertaken with a view to studying the formation of double compounds of these iodides in organic solvents.

Experimental

The compounds were all of Merck's E.P. quality and the solvents were dehydrated and distilled. Two sets of experiments under similar conditions in each case were carried out. The results reported are an average of the two values. A measured volume of the solvent was taken in each of the flasks, the components were added alternately till the solution was saturated with respect to both at room temperature (about 25°) and left overnight. It was filtered and the filtrate kept in a vacuum desiccator over $CaCl_2$ in the case of alcohol and over CaO, when acetone was used as the solvent. It took a long time for crystallisation. As the products decomposed slightly on recrystallisation, these were washed once with a minimum quantity of the solvent, filterpressed, dried in a desiccator and examined.

Standard methods of separation and estimation were used. Mercury was estimated as HgS, cadmium as pyrophosphate, strontium as sulphate, iodine as AgI and nitrogen by Kjeldahl's method. Calcium was precipitated as oxalate and determined volumetrically by dissolving it in dilute H_2SO_4 and titrating it against standard $KMnO_4$ solution. In compounds containing mercury and iodine together, the following

procedure for the estimation of iodine was adopted (Caul and Schoonover, *J. Res. Nat. Bur.*, 1941, **26**, 481). A known quantity of the substance was heated with 15-20% NaOH solution on a water-bath at about 50°, 1 or 2 c.c. of formaldehyde added to it and heating continued for about half an hour when HgI_2 was reduced completely to metallic mercury. The contents were filtered and washed several times with water. The filtrate and washings were mixed and iodine was estimated as AgI. Nitrogen in the amide compound was estimated by Kjeldahl's method and the nitrogen in pyridire compounds, by heating the substance with about 40% NaOH solution, absorbing the distilled pyridine into a known volume of standard H_2SO_4, and back-titrating the excess acid with a standard NaOH solution, using methyl orange as indicator (cf. Allen, "Commercial Organic Analysis", 1911, Vol. III, pp. 318-19).

The method of preparation and the properties of the compounds being closely similar, the results are recorded in Table I.

TABLE I

Compound formed.	Characteristic properties.	Found.	Calc.
Alcoholo ammonium tri-iodo-mercuriate $NH_4I.HgI_2.C_2H_5OH$	Deep yellow needles ; hygroscopic ; decomposing when treated with a large quantity of water or the solvent.	N : 2.13% Hg : 30.98 I : 59.12	2.17% 31 00 59.00
Hexa-alcoholo lithium tetra-iodo-mercuriate $2LiI.HgI_2\ 6C_2H_5OH$	Do	Hg : 19.94 I : 50.94	20 09 50.86
Di-alcoholo sodium tri-iodo-mercuriate $NaI\ HgI_2.2C_2H_5OH$	Yellow plates ; other properties as above.	Hg : 28.78 I : 54 69	28.81 54.68
Diacetono sodium tri-iodomercuriate $NaI.HgI_2.2CH_3COCH_3$	Do ; very hygroscopic.	Hg : 27.77 I : 52.70	27 84 52.86
Diacetic acido sodium tri-iodo-mercuriate $NaI.HgI_2.2HOAc$	Do	Hg : 27.58 I : 52.63	27.69 52.56
Dialcoholo potassium tri-iodo-mercuriate $KI.HgI_2.2C_2H_5OH$	Do ; less hygroscopic than the Na salt.	Hg : 27.96 I : 53.54	28.15 53.44
Dipyridino potassium tri-iodo-mercuriate $KI.HgI_2.2Py$	White crystalline compound ; loses pyridine on exposure to the atmosphere and asssumes a yellowish tinge.	Hg : 25.65 N : 3 48 I : 48.85	25.77 3.59 48.90
Ammonium tetra-iodo cadmiate $2NH_4I\ CdI_2$.	White, slightly hygroscopic, crystalline mass, decomposing in water.	N : 4.23 Cd : 17.09 I : 77.39	4.27 17.12 77.37
Alcoholo ammonium tri-iodocadmiate (crystallised from the mother-liquor at 0°) $NH_4I.CdI_2\ C_2H_5OH$.	Do	N : 2.49 Cd : 20.11 I : 68 18	2.51 20.17 68.15
Potassium tetra-iodocadmiate $2KI.CdI_2$	Do ; non-hygroscopic.	Cd : 16.04 I : 72 75	16.09 72.68

TABLE I (contd.)

Compound formed	Characteristic properties.	Found.	Calc.
Octo-alcoholo magnesium tetra-iodomercurate (from a soln. of the composition $MgI_2+1.878HgI_2+16$ alcohol and sp. gr. 2.22 at 25°) $MgI_2.HgI_2.8C_2H_5OH$	Yellow; very hygroscopic; prismatic crystals; similar in nature to the alkali metal compounds.	Hg: 18.09 I: 46.26	22.23 46.13
Calcium hexa-iodomercuriate $CaI_2.2HgI_2$	Do	Hg: 33.22 I: 63.32 Ca: 3.28	33.32 63.32 3.30
Hexa-alcoholo calcium octo-iodomercuriate (from the mother-liquor when it was saturated with HgI_2 and cooled at 0°) $CaI_2.3HgI_2.6C_2H_5OH$	Do	Hg: 31.22 I: 52.65	31.13 52.50
Strontium hexa-iodomercuriate $SrI_2.2HgI_2$	Do	Hg: 32.05 I: 60.72 Sr: 6.77	32.13 60.10 7.00
Cadmium octo-iodomercuriate $CdI_2.3HgI_2$.	Yellow, non-hygroscopic, crystalline compound: other properties as above.	Hg: 34.62 Cd: 6.41 I: 58.68	34.78 6.49 58.70
Deca-acetamido cadmium hexa-iodomercuriate $:CdI_2.HgI_2.10CH_3CONH$	Yellow, non-hygroscopic crystals, m.p. 85-85.5°; soluble in water, alcohol and acetone.	N: 7.75 Hg: 11.20 Cd: 12.82 I: 42.92	7.87 11.28 12.64 42.80
* Hexapyridino cadmium iodide, $CdI_2.6Py$	White crystalline compound, m.p. 108-109°; dissolves in hot water.	N: 9.91 Cd: 13.31 I: 30.26	9.99 13.37 30.22
Dipyridino mercuric iodide, $HgI_2.2Py$	White crystalline mass, m.p. 110°-12°; loses pyridine on exposure to the atmosphere.	N: 4.52 Hg: 32.66 I: 41.40	4.57 32.75 41.47

* The last but one compound was obtained when a mixture of HgI_2 and CdI_2 was dissolved in warm pyridine and allowed to cool at the room temperature (25°) or to an alcoholic solution of these iodides pyridine was added at the room temperature.

On crystallising the mother-liquor at 0° for 24 hours, the last compound separated out.

The last two compounds in Table I were obtained when HgI_2 or CdI_2, alone, was treated with pyridine. It appears that after being fully saturated with the maximum number of pyridine molecules, no binding forces are available to form the double compound.

In the case of benzamide, when the mixture of the two iodides was dissolved in the molten solvent, it formed a yellow clear solution, but on solidifying, a waxy mass containing free HgI_2 was obtained. When a mixture of these iodides and benzamide was dissolved in alcohol and kept at 0° for some time, a yellowish crystalline mass, which turned white on washing with alcohol and approximating roughly to $CdI_2.6$ benzamide (Found: Cd, 10.66; N, 7.65. Calc. for $CdI_2.5\,7\,C_6H_5CONH_2$: Cd, 10.7; N, 7.6%), m.p. 108°-10° (not sharp), was formed. The mother-liquor, when concentrated, yielded pure HgI_2 and no double compound.

There could be obtained no double compound with Li or Na iodide and CdI_2 in any condition.

From the above experiments it appears that the solubility of CdI_2 or HgI_2 in organic solvents is increased to a considerable extent in presence of alkali or alkaline earth metal iodides; HgI_2 dissolves to a far greater extent in presence of CdI_2 in these media. The compounds formed are similar to those obtained in aqueous medium and generally crystallise with a few molecules of the solvent.

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DIAMAGNETIC SUSCEPTIBILITY OF ORGANO-METALLIC COMPOUNDS. PART I. ANTIMONY COMPOUNDS

By N. K. Parab and D. M. Desai

The diamagnetic susceptibilities of organo-antimony compounds, R_3Sb, and their dihalides, R_3SbX_2, have been determined by a modified form of Gouy's method. The results show that the susceptibility of antimony atom, deduced from trivalent compounds, is higher than the value deduced from pentavalent compounds. The difference in the susceptibility of tri- and pentavalent antimony has been xplained on the basis of the difference in the structure of these compounds. The theoretically calculated values of $\chi_{Sb^{III}}$ and $\chi_{Sb^{V}}$ by Slater's and Angus' methods have been compared with the observed values for tri- and penta-valent Sb atom.

The present investigation deals with a study of the diamagnetic susceptibility of a series of organo-antimony compounds of the type R_3Sb and their dihalides, R_3SbX_2. It appears from the literature that only a few organo-metallic compounds of antimony have been studied by Pascal (*Compt. rend.*, 1921, **173**, 144, 712; 1922, **174**, 437, 1698 1922, **175**, 106_3) who deduced therefrom the susceptibility of antimony atom.

Experimental

The triarylstibines R_3Sb, and their dihalides, R_3SbX_2, were prepared by the methods, already reported in the literature. Pure chemicals were used in the preparation and the crude products obtained were purified by repeated crystallisations. The purity of the compounds was established from the melting points and the percentage metal contents found by chemical analysis. In the case of dihalides, the close agreement of the observed and the reported melting points was taken as a criterion of purity, as these compounds were found difficult to decompose.

The diamagnetic susceptibility of these compounds was determined by a modified form of Gouy's method (*ibid.*, 1889, **109**, 935), and the susceptibility values were calculated by using the following equation (cf. Angus and Tilsten, *Trans. Faraday Soc.*, 1947, **43**, 235):

$$\chi = \frac{\alpha F + C}{w}$$

where

$$\alpha = \frac{2l}{H_1^2 - H_2^2}$$

and $C = V \times K_m$ (volume susceptibility of air being taken as $K_m = 0.029 \times 10^{-6}$).

The calibration of the apparatus was made by using pure benzene (free from thiophene), susceptibility value of which is accurately known to be $\chi = -0.702 \times 10^{-6}$ (cf. Angus and Hill, *ibid.*, 1943, **39**, 185; Baddar, Hilal and Sugden, *J. Chem. Soc.*, 1949, 1, 132).

The results of the diamagnetic susceptibility measurements are reported in Table I in which χ_s represents the specific susceptibility and χ_M, the molar susceptibility values. These values are the mean of at least three independent determinations and these have been represented in terms of -1×10^{-6} c.g.s. units.

TABLE I

No.	Compounds.	Formula.	χ_s.	χ'_M.	χ_E.	χ^{Sb}.
1.	Triphenylstibine	$(C_6H_5)_3Sb$	0.5169 ± 0.004 0.5 6 (P)*	182.3	156.27	26 03
2.	Tri-*p*-tolylstibine	$[p\text{-}Me.C_6H_4]_3Sb$	0 5484 ± 0.003	216.6	191.85	24.75
3.	Tri-*m*-xylylstibine	$[m\text{-}Me_2C_6H_3]_3Sb$	0.5750 ± 0.003	251.1	227.43	23.67
4.	Tri-*p*-anisylstibine	$[p\text{-}OMe.C_6H_4]_3Sb$	0 5198 ± 0 003	230.1	205.68	24.42
5.	Tri-*p*-phenetylstibine	$[p\text{-}ORt.C_6H_4]_3.Sb$	0.5486 ± 0.003	265.9	241.26	24.64
6.	Triphenylstibine dichloride	$(C_6H_5)_3SbCl_2$	0.5077 ± 0.003	215.1	196.47	18.63
7.	Tri-*p*-tolylstibine dichloride	$(p\text{-}Me.C_6H_4)_3SbCl_2$	0.5351 ± 0.003	249.2	232.05	17.15
8.	Tribenzylstibine dichloride	$(C_6H_5CH_2)_3SbCl_2$	0.5359 ± 0 003	249.6	232.05	17.55
9.	Triphenylstibine dibromide	$(C_6H_5)_3SbBr_2$	0.4532 ± 0.003	232.4	217.47	14.93
10.	Tri-*p*-tolylstibine dibromide	$(Me.C_6H_4)_3SbBr_2$	0.4821 ± 0.002	267.4	253.05	14.35
11.	Tri-*m*-xylylstibine dibromide	$[Me_2C_6H_3]_3SbBr_2$	0.5040 ± 0.003	300.7	288.63	12.07
12.	Triphenylstibine di-iodide	$(C_6H_5)_3SbI_2$	0.4303 ± 0.003	261.1	245.47	15.63
13.	Tri-*p*-tolylstibine di-iodide	$(Me.C_6H_4)_3SbI_2$	0.4551 ± 0.003	295.3	281.05	14.25

* Pascal, *loc. cit.*

DISCUSSION

Susceptibility of Tri- and Pentavalent Antimony Atom.—The susceptibility values of tri- and pentavalent antimony atom were deduced from the corresponding molar susceptibilities of triaryl compounds and their dihalides respectively, using Pascal's values of constituent atoms and constitutive correction constants (cf. Bhatnagar and Mathur, "Physical Principles and Applications of Magneto chemistry, 1935, pp. 90-93). These values of $\chi_{Sb^{III}}$ and $\chi_{Sb^{V}}$, deduced from the corresponding compounds, are shown in the last column of Table I.

It will be seen that the susceptibility values of tri- and pentavalent Sb atom agree well with each other, in each case; the average values of $\chi_{Sb^{III}}$ and $\chi_{Sb^{V}}$ found being -24.70×10^{-6} and -15.50×10^{-6} respectively. It is obvious that these values of tri- and pentavalent antimony atoms are inclusive of the effects of C—Sb and Sb—halogen, as the case may be. The difference in the values for $\chi_{Sb^{III}}$ and $\chi_{Sb^{V}}$

appears to be due to the difference in the structure of these two types of compounds. The triarylstibines are probably pyramidal like many trivalent antimony compounds, such as, antimony trichloride, tribromide and tri-iodide (Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, **176A**, 153). The Raman spectra of trimethylstibine (Rosenbaum *et al.*, *J. Chem. Phys.*, 1940, **8**, 366) and the dipole moment of triphenylstibine (Bergmann and Schutz, *Z. physikal. Chem.*, 1932, **B19**, 401) also favour the pyramidal structure for these compounds. The addition of two halogen atoms to the triarylstibine changes the covalency of antimony from three to five and the resulting structure is a trigonal bipyramid, as established from the physical properties of the dihalides. The crystal structure of only trimethylstibine dihalides appears to have been investigated so far (Wells, *Z. Krist.*, 1938, **99**, 367). The results indicate that this compound has a trigonal bipyramidal structure with two halogen atoms in the polar position and at a distance from the central antimony atom, intermediate between that required for electrovalent and covalent bonds. Triphenylstibine dichloride (Jensen, *Z. anorg. allgem. Chem*, 1943, **250**, 257) has been found to have a zero dipole moment, as is to be expected from the trigonal bipyramid, and linking between central atom and halogen atom appears to be strongly polar in this compound. All these evidences indicate that antimony in R_3SbX_2 is pentavalent as opposed to trivalent antimony in R_3Sb and that antimony has a greater positive charge in the dihalides than in the triarylstibines. This positive charge arises from the strongly polar character of Sb—halogen bonds. It is obvious therefore that as a consequence of the greater positive charge on the antimony in dihalides, χ_{Sb} value would be smaller in these compounds than in the case of triaryl compounds.

Kido (*Sci. Rep. Tohoku Imp. Univ.*, 1932, **21**, 869) had made an interesting observation in the susceptibility values of atoms which showed more than one valency. He found that the observed difference in the susceptibility of atoms like P, As, Cl in trivalent and pentavalent states was of the order of 8-10 units. The observed difference in the susceptibility of antimony in tri- and pentavalent states is about 9 units, which is in agreement with the observation of Kido.

Comparison of Observed Values of χ_{Sb} with Theoretically Calculated Values.—The following table shows the theoretically calculated values of $\chi_{Sb^{3+}}$ and $\chi_{Sb^{5+}}$ due to Slater (*Phys. Rev.*, 1930, **36**, 57) and Angus (*Proc. Roy. Soc.*, 1932, **136A**, 569) along with the observed values for $\chi_{Sb^{III}}$ and Sb^{V}.

TABLE II

χ_{Sb} values.

	Observed.	Calculated.	
		Slater.	Angus.
Trivalent	24.70	30.60	30.45
Pentavalent	15.50	20.07	19.03

It is seen that the theoretical values, calculated by Slater's and Angus' methods, are both higher by 5-6 units than the observed values in each case. In the triaryl-

stibines, the link between Sb and C will be essentially covalent, although it may have a certain ionic character. From the difference in the electronegativities of Sb and C, the ionic character of this link is estimated to be about 15%. The departure of the theoretically calculated $\chi_{Sb^{3+}}$ values from the value deduced from trivalent compounds may be due to the formation of Sb—C bonds. Similarly, the observed difference between the calcutated value of $\chi_{Sb^{5+}}$ and the value deduced from pentavalent compounds may be attributed to the bond effects due to Sb—C and Sb—halogen bonds.

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DIAMAGNETIC SUSCEPTIBILITY OF ORGANO-METALLIC COMPOUNDS. PART II. BISMUTH COMPOUNDS

By N. K. Parab and D. M. Desai

The diamagnetic susceptibilities of some organo-bismuth compounds, R_3Bi, and their dichlorides, R_3BiCl_2, have been determined by a modified form of Gouy's method. The results show that the susceptibility of bismuth atom, deduced from trivalent and pentavalent compounds, differ by about 7 units. The difference observed in χ_{Bi} values from trivalent and pentavalent compounds may be due to the difference in the structure of these two types of compounds. The susceptibility of $\chi_{Bi^{3+}}$ and $\chi_{Bi^{5+}}$ have been theoretically calculated using Slater's and Angus' methods compared with χ_{Bi} values deduced from trivalent and pentavalent compounds.

In continuation of the work reported earlier (this *issue*, p. 569), the diamagnetic susceptibility of some organo-bismuth compounds of the type R_3Bi and R_3BiX_2 has been studied in this investigation. Only one compound, namely, triphenylbismuthine, has been studied so far (cf. Pascal, *Compt. rend.*, 1921, **173**, 144, 1712; 1922, **174**, 437, 1898; 1922, **175**, 1063).

Experimental

The compounds studied in this investigation were prepared by the known methods and were purified by repeated crystallisations before measurements. Their melting points and the percentage metal contents were determined to establish their purity. In the case of dihalides, the close agreement between the observed and the reported melting points was taken as the criterion of purity, as those compounds were found difficult to decompose.

The diamagnetic susceptibility of these compounds were determined and calculated as reported in Part I (*loc. cit.*). The results of the susceptibility measurements are shown in Table I. These values are the mean of at least three independent determinations (in terms of -1×10^{-6} c.g.s. units).

Table I

No.	Compounds.	Formula.	χ_a.	χ_M.	χ_a.	χ_{Bi}.
1	Triphenylbismuthine	$(C_6H_5)_3Bi$	0.4422 ± 0.003	194.6	156.27	38.33
2	Tri-*p*-tolylbismuthine	$[p\text{-}CH_3.C_6H_4]_3Bi$	0.4755 ± 0.003	229.2	191.85	37.35
3	Tri *m*-xylylbismuthine	$[m\text{-}(CH_3)_2.C_6H_3]_3Bi$	0.5013 ± 0.003	262.7	227.43	35.27
4	Triphenylbismuthine dichloride	$(C_6H_5)_3BiCl_2$	0.4457 ± 0.003	227.7	196.47	31.23
5	Tri-*p*-tolylbismuthine dichloride	$(CH_3.C_6H_4)_3BiCl_2$	0.4764 ± 0.003	263.4	232.05	31.35
6	Tri-*m*-xylylbismuthine dichloride	$(CH_3)_2C_6H_3BiCl_2$	0.4983 ± 0.003	296.5	267.63	28.87

DISCUSSION

Only one compound, namely, triphenylbismuthine, was studied by Pascal (*loc. cit.*) who obtained the specific susceptibility value as -0.447×10^{-6}. The value obtained by us is in close agreement with this reported value.

Susceptibility of Tri- and Pentavalent Bismuth.—The triphenylbismuthine may be looked upon as the substitution product of H_3Bi which contains trivalent bismuth. The susceptibility of trivalent bismuth has been deduced from the molar susceptibilities of triarylbismuthines. Pascal's values (cf. Bhatnagar and Mathur, "Physical Principles and Applications of Magneto-chemistry", 1935, pp. 90-93) of various atoms and constitutive correction constants were used to calculate the susceptibility of the organic part of the molecule (χ_R). Triarylbismuthine dihalides are the addition products obtained by adding two halogen atoms to the corresponding triaryl compound. These compounds therefore contain pentavalent bismuth atom. The susceptibility of pentavalent bismuth has been deduced from the molar susceptibilities of the triarylbismuthine dichloride by using Pascal's values (*loc. cit.*) of various atoms other than bismuth and the relevant constitutive correction constants (χ_R). These values of trivalent and pentavalent bismuth atom, deduced from the corresponding compounds, are shown in the last column of Table I.

It will be seen that the susceptibility values of trivalent bismuth atom, deduced from the triarylbismuthines, agree very closely with each other, the average value being found as -36.98×10^{-6}. This value represents the susceptibility of trivalent bismuth in compounds of the type R_3Bi. Similarly, it has been observed that the susceptibility of pentavalent bismuth atom, deduced from dichlorides, are very near each other, the average value being found as -30.48×10^{-6}, which represents the susceptibility of pentavalent bismuth atom in compounds of the type R_3BiX_2. It is obvious that these values of tri- and pentavalent bismuth atom are inclusive of the bond effects due to C—Bi and Bi—halogen linkages, as the case may be.

It will be seen, on comparison, that the susceptibility of trivalent bismuth atom, deduced from triarylbismuthines, is lower than that of pentavalent bismuth atom, deduced from dihalides, by about 7.0 units. A similar difference was also observed in the susceptibility value of antimony in trivalent and pentavalent compounds of the type R_3Sb and R_3SbX_2. These results therefore support the observation of Kido (cf. Part I, *loc. cit.*). The observed difference in the susceptibility of bismuth atom in these two types of compounds may possibly be due to the difference in the structure of these compounds. Bergmann and Schutz (*Z. physikal. Chem.*, 1932, **B19**, 401) have studied the dipole moment of triphenylbismuthine and from the zero value of dipole moment of this compound, they have concluded that its structure is that of a plane triangle with bismuth atom situated at the centre of gravity. The addition of two halogen atoms to the triarylbismuthine changes the covalency of bismuth from 3 to 5 and like the dihalides of triarylstibines, the triarylbismuthine dichloride may have a trigonal bipyramidal structure. Jenson (*Z. anorg. allgem. Chem.*, 1943, **250**, 257) observed that the molecular polarisation of triphenylbismuthine dichloride was in-

dependent of temperature. It has accordingly a zero dipole moment which shows that the molecule possesses the configuration of a trigonal bipyramid. The large atomic polarisation in this compound also indicates that the binding between the central atom and the halogen atom is strongly polar. The halogens in R_2BiX_2 compounds have also been found to be quite labile and undergo double decomposition readily (cf. Gillman and Yale, *Chem. Rev.*, 1942, **30**, 304). All these evidences show that bismuth has a greater positive charge in the dihalides than in triaryl compounds. It is obvious therefore that as a consequence of the greater positive charge on the bismuth atom in dihalides, χ_{Bi} values would be smaller in these compounds than in triaryl compounds.

Comparison of Observed χ_{Bi} with the Theoretically Calculated Values.—The susceptibility values of Bi^{3+} and Bi^{5+} have been calculated by using Slater's (*Phys. Rev.*, 1930, **36**, 57) and Angus' (*Proc. Roy. Soc.*, 1932, **136A**, 569) methods and these theoretically calculated values together with the values deduced from trivalent and pentavalent compounds are recorded in Table II.

TABLE II

	χ_{Bi} values.		
	Obs.	Calc.	
		Slater.	Angus.
Trivalent	36.98	41.35	41.29
Pentavalent	30.48	28.74	28.68

It is observed that χ_{Bi} value, deduced from trivalent compounds, is lower than the theoretically calculated value by about 5 units, while that obtained from pentavalent compounds is in good agreement with the calculated values. The theoretical values are for free Bi^{3+} and Bi^{5+} ions. In the triarylbismuthine, the link between Bi—C will be essentially covalent, although it may have a certain ionic character. The difference in the electronegativities of Bi and C will be greater than that in the case of Sb and C. The departure of the theoretically calculated $\chi_{Bi^{3+}}$ values from the value deduced from trivalent compounds may thus be due to the formation of Bi—C links. It is found that χ_{Bi} value obtained from pentavalent bismuth compounds agrees more closely with the calculated value for Bi^{5+}, using Slater's and Angus' methods, than the corresponding value for $\chi_{Sb^{V}}$ agrees with $\chi_{Sb^{5+}}$, calculated by these methods. This may be due to the greater ionic character of Bi—C and Bi—Cl linkages as compared with the Sb—C and Sb—Cl linkages.

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PREPARATION OF SOME 3-ARYL 2-ARYLIMINOTHIAZOLID-4-ONES AND THEIR DERIVATIVES

By Ravindra Pratap Rao

Five 3-aryl-2-aryliminothiazolid-4-ones have been prepared by condensing *S*-diarylthioureas with monochloroacetic acid in presence of anhydrous sodium acetate; their 5-benzylidene and 5-(*p*)-sulphonamidophenylazo derivatives have also been described.

The imporatance of thiazolidone compounds as potent medicinals and amoebacidal agents has encouraged the author to synthesise several 3-aryl-2-aryliminothiazolid-4-ones and prepare their derivatives. The present work is in continuation with the earlier work of Bhargava (*J. Amer. Chem. Soc*, 1951, **73**, 2353) and Bhargava *et al.* (this *Journal*, 1955, **32**, 49, 763).

In the present investigation five different 3-aryl-2-aryliminothiazolid-4-ones have been prepared according to the procedure adopted in the preparation of 3-*o*-anisyl-2-*o*-anisyliminothiazolid-4-one (vide Experimental).

The thiazolidone compounds, prepared above, were condensed with benzaldehyde in glacial acetic acid medium in presence of anhydrous sodium acetate for the preparation of the 5-benzylidene derivatives of the thiazolidones, but it was found that due to the presence of acidic medium, some thiazolidones were hydrolysed to thiazolid-2:4-diones, and both these compounds reacted with benzaldehyde to form their benzylidene derivatives. As the separation of these derivatives was very difficult, it was thought best to avoid the use of acidic medium, and the thiazolidone compounds were refluxed with an excess of benzaldehyde without any solvent, using pyridine as the condensing agent. The derivatives, thus prepared, had no chance to be contaminated with benzylidene derivatives of the corresponding thiazolid-2:4-diones. Further, the thiazolidone compounds have been coupled with diazotised sulphanilamide to give rise to 5-(*p*)-sulphonamidophenylazo derivatives. The fact that the azo group is attached to the reactive methylene group at position 5 of the thiazolidone nucleus has been reported earlier (Rout, this *Journal*, 1955, **32**, 563; Bhargava *et al.*, *ibid.*, 1956, **33**, 596).

Experimental

S-Diarylthioureas were obtained by the conventional method of Rathke (*Ber.*, 1873, **5**, 799). In the preparation of *S*-di-*o*-chlorophenylthiourea, the yield obtained was very small due to the formation of *o*-chloroaniline salt of phenythiocarbamic acid of the formula $C_6H_4Cl.NH.CS.SH(NH_2C_6H_4Cl)$ (Grosch, *Ber.*, 1899, **32**, 1088). However, after washing several times with hot water, the latter was dissolved out and the pure thiourea left over. Similarly *S*-di-*m*-chlorophenylthiourea was also obtained in low yield.

3-*o*-*Anisyl*-2-*o*-*anisyliminothiazolid*-4-*one*.—*S*-Di-*o*-anisylthiourea (3.6 g.) was heated under reflux with monochloroacetic acid (1.5 g.) in presence of anhydrous sodium acetate (1.6 g.) and absolute alcohol (20-25 c.c.) on a water-bath for 4 hours. The reaction mixture was then poured in water, when a precipitate was obtained. It was filtered, washed several times with boiling water, and finally recrystallised from alcohol, m.p. 197°, yield 80%. The analytical results of this and other thiazolidones are recorded in Table I.

TABLE I

3-*Aryl* (R)-2-*aryl* (R)-*iminothiazolid*-4-*ones*.

Compd. No.	Nature of R.	Formula.	M.P.	% Yield.	% Nitrogen. Found.	Calc.
1	*o*-Anisyl	$C_{17}H_{16}O_3N_2S$	157°	80	8.93	8.53
2	*o*-Phenetyl	$C_{19}H_{20}O_3N_2S$	110°-19°	82	8.05	7.86
3	*o*-Chlorophenyl	$C_{15}H_{10}ON_2Cl_2S$	170-71°	68	7.97	8.30
4	*m*-Chlorophenyl	$C_{15}H_{10}ON_2Cl_2S$	135°	76	8.11	8.30
5	*p*-Chlorophenyl*	$C_{15}H_{10}ON_2Cl_2S$	165°	85	8.09	8.30

* Dains, Irvin and Harrel (*J. Amer. Chem. Soc.*, 1921, **43**, 613) also report its m.p. as 165°.

5-*Benzylidene*-3-*o*-*anisyl*-2-*o*-*anisyliminothiazolid*-4-*one*.—The preceding 3-*o*-anisylthiazolidone (1 g.) and benzaldehyde (1.5 c.c.) were refluxed in presence of pyridine (5 c.c.) in an oil-bath at 150-60° for 5 to 6 hours. The clear solution thus obtained, was cooled and HCl (dil.) was added to it in excess, when a precipitate was obtained. After shaking well and allowing the precipitate to stand overnight, the greenish yellow precipitate was filtered off, washed with hot water several times till free from acid, and finally it was crystallised from alcohol, m.p. 160°, yield 84%. The properties and analytical results are reported in Table II.

TABLE II

5-*Benzylidene*-3-*aryl*-2-*aryliminothiazolid*-4-*ones*.

Compd. No.	Formula.	Colour.	M.P.	% Yield.	% Nitrogen. Found.	Calc.
1	$C_{24}H_{20}O_3N_2S$	Greenish yellow	160°	84	6.65	6.73
2	$C_{26}H_{24}O_3N_2S$	Brownish grey	143-44°	58	6.50	6.30
3	$C_{22}H_{14}ON_2Cl_2S$	Pale grey	169-70°	75	6.81	6.58
4	$C_{22}H_{14}ON_2Cl_2S$	Yellow	172°	70	6.74	6.58
5	$C_{22}H_{14}ON_2Cl_2S$*	Greenish yellow	212	92	6.90	6.58

* Also prepared by Dains *et al.* (*loc. cit.*), m.p. 213°.

5-(p)-*Sulphonamidophenylazo*-3-o-*anisyl*-2-o-*anisyliminothiazolid*-4-*one*.—Sulphanilamide (0.56 g.) was dissolved in acetic acid (5 c.c.), HCl (conc., 5 c.c.) and water (10 c.c.). This was kept in an ice-bath and diazotised with sodium nitrite (0.5 g.) in minimum quantity of water. The diazotised sulphanilamide was added slowly to a precooled solution of 3-*o*-anisyl-2-*o*-anis/limiuothiazolid-4-one (0.5 g.) in acetone (5 c.c.) and glacial acetic acid (12-15 c.c.) with constant stirring. The reaction mixture was stirred for 15 minutes more and then poured on ice, contained in a beaker, and shaken well. The beaker was kept aside overnight when a bright yellow precipitate came out. It was filtered, washed with hot water, dried and crystallised from alcohol, m.p. 183°, yield 57%. The properties and analytical data are recorded in Table III.

TABLE III

5-(p)-*Sulphonamidophenylazo*-3-*aryl*-2-*aryliminothiazolid*-4-*ones*.

Compd. No.	Formula.	Colour.	M.P.	% Yield.	% Nitrogen. Found.	Calc.
1	$C_{23}H_{21}O_5N_5S_2$	Bright yellow	183°	57	13.56	13.69
2	$C_{25}H_{25}O_5N_5S_2$	Deep ,,	145-50° (decomp.)	62	13.12	12.98
3	$C_{21}H_{15}O_3N_5Cl_2S_2$	Light yellow	168°	53	13.59	13.46
4	$C_{21}H_{15}O_3N_5Cl_2S_2$	Deep orange	125°	69	12.98	13.46
5	$C_{21}H_{15}O_3N_5Cl_2S_2$	Brown-yellow	156-58°	61	13.60	13.46

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DECOMPOSITION OF HYDROGEN PEROXIDE IN HOMOGENEOUS MIXTURES

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The homegeneous decomposition of decinormal hydrogen peroxide in presence of a number of salts has been studied mostly at 35°. It is found that no cation is a catalyst unless it can exist in two states of oxidation. A simple mechanism of decomposition involving activated hydrogen peroxide molecules (but no free radicals) has been suggested which explains the first order decomposition with respect to the peroxide and the lowering of the corresponding velocity constant at low concentrations.

From the survey of the work done on the characteristics of decomposition of H_2O_2 in solution in presence of homogeneous as well as heterogeneous catalysts, the decomposition appears to be suppressed to a larger or smaller degree by hydrogen ions, in both cases. The soluble catalysts, limited in number, are almost invariably cations, capable of existence in more than one oxidised state, e.g., iron, copper and manganese ions. Bromine is also a good catalyst and is an example of an anion. On the other hand, heterogeneous catalysts are numerous (Thenard, *Ann. chim. phys.*, 1818, *ii*, **9**, 441, et seq, quoted by Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. **1**, p. 936, 1935, London).

Oxygen gas is evolved, and therefore water must be the other product of decomposition. In the absence of a catalyst, although the rate is greatly reduced, the reaction is still possible ; it is depressed by H^+ and accelerated by OH^-. It appears that the simplest mechanism, which corresponds to these reactions, can be expressed as:

$$H_2O_2 \rightarrow 2H^+ + O_2^{2-} \quad \ldots \quad (a)$$

$$O_2^{2-} + H_2O_2 \rightarrow 2OH^- + O_2 \quad \ldots \quad (b)$$

$$2H_2O_2 \rightarrow O_2 + (2H^+ + 2OH^-) \quad \ldots \quad (c)$$

When two molecules of H_2O_2 react, one molecule of oxygen and two molecules of water are produced. The ionisation (*a*) may, of course, take place in two steps, and it being a simple ionisation is expected to be much faster than (*b*), so that increase of $[H^+]$ will depress $[O_2^{2-}]$, thereby depressing the rate at which oxygen is evolved. The ionisation (*a*) must be quite small since the conductivity of aqueous hydrogen peroxide is reported to be small, although the results are not conclusive since it is difficult to find a suitable electrode (Newton Friend, "Text Book of Inorganic Chemistry", Vol. VII, Part I, p. 332, 1924, London).

Presence of catalysts like Fe^{3+} greatly increases the rate of decomposition even when stabilisers are present. Perhaps the simplest mechanism to account for the same can be expressed as follows :

$$H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-} \quad \ldots \quad (a')$$
$$2Fe^{3+} + O_2^{2-} \rightarrow O_2 + 2Fe^{2+} \quad \ldots \quad (b')$$
$$2Fe^{2+} + H_2O_2 \rightarrow 2OH^- + 2Fe^{3+} \quad \ldots \quad (c')$$
$$2H_2O_2 \rightarrow O_2 + (2H^+ + 2OH^-) \quad \ldots \quad (d')$$

(b') is again a reaction between ions and likely to be fast, but (c') is not such a reaction. It appears that (c') should determine the overall rate in this case. In the uncatalysed reaction, the discharge of O_2^{2-} and the production of OH^- ions (which remove hydrogen ions produced in *a*) take place in the same step, the reaction involving H_2O_2. In the catalysed reaction, they take place in two different steps, the reactions involving Fe^{3+} and Fe^{2+} ions.

On the other hand, Haber and Weiss (*Proc. Roy. Soc.*, 1934, **A147**, 332) consider a more complicated mechanism necessary for the reaction. The mechanism involves production of free radicals, OH and HO_2. Thus, for the decomposition catalysed by ferrous ions they conclude that

$$H_2O_2 + Fe^{2+} \rightarrow OH + OH^- + Fe^{3+} \quad \ldots \quad (i)$$
$$OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad \ldots \quad (ii)$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad \ldots \quad (iii)$$
$$HO_2 + H_2O_2 \rightarrow OH + O_2 + H_2O \quad \ldots \quad (iv)$$
$$HO_2 \rightleftharpoons O_2^- + H^+ \quad \ldots \quad (v)$$
$$O_2^- + H_2O_2 \rightarrow O_2 + OH^- + OH \quad \ldots \quad (vi)$$

When excess H_2O_2 is present, the reaction goes beyond oxidation of Fe^{2+}, and O_2 is produced. When one starts with Fe^{3+} ions as catalysts, some of them are first reduced,

$$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2 \quad \ldots \quad (vii)$$

after which oxygen is evolved according to the previous mechanism. Barb *et al.* (*Trans. Faraday Soc.*, 1951, **47**, 475, 593) agree that the free radicals-OH, HO_2^- are formed, but consider that oxygen is evolved not by reaction (*iv*) or (*vi*) but as

$$HO_2 + Fe^{3+} = O_2 + Fe^{2+} + H^+.$$

If this mechanism is substantially correct, it should be unlikely to come across an ion catalyst which does not have two oxidation states. A search of the literature did not produce a very clear picture. We presume that the vagueness is due to self-decomposition of H_2O_2, even when mildly stabilised, and different experimenters having used different conditions. Consequently, we decided to examine a number of salts at the same concentration of peroxide, keeping other conditions also as similar as possible.

EXPERIMENTAL

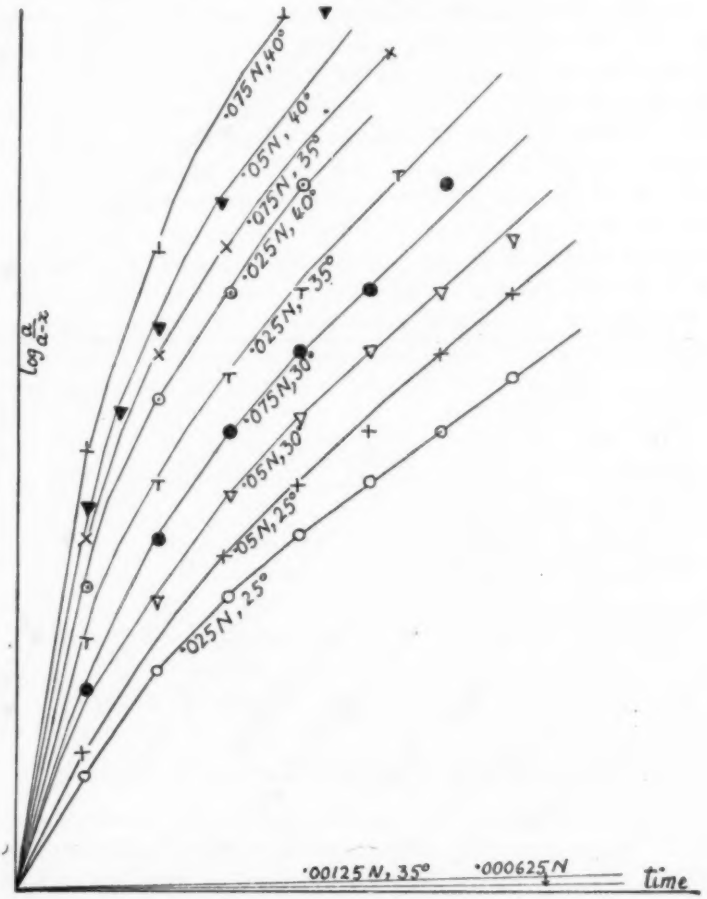
Catalytic Decomposition by Ferric Sulphate

Although a good deal of work was done on the role of ferric salts as catalysts, in view of the very rapid hydrolysis of these salts at low concentrations (Mellor, *loc. cit.*, Vol. **14**, pp. 46, 51 et seq; Gyani and Misra, this *Journal*, 1954, **31**, 499), we were curious to know what would happen if the salt concentrations were greatly reduced.

Stock solutions of normal ferric sulphate and 0.4N-H_2O_2 were prepared. Peroxide (25 c.c.) was taken in a volumetric flask, ferric sulphate (50 c.c.) added to it and the mixture was then diluted to 100 c.c. Ten c.c. portions of the mixture were withdrawn after 10, 20 ..... 120 minutes and titrated with $N/10$-$KMnO_4$. Similar other experiments were performed in which the volume of ferric sulphate was decreased to 5, 2.5, 1.25, 0.5, 0.25 and 0.125 c.c. The rate of decomposition at 35° was found rapid so long as the mixture was at least 0.125 N with respect to ferric sulphate, over 80% decomposing in the first 20 minutes. Less than 2% was left after 100 mins.

FIG. 1

Catalysis by Ferric sulph. solns.



As the concentration of the salt was further decreased, there was a rapid fall in the rate (vide Fig. 1). The catalytic activity enormously decreases as one goes from 0.005 N to 0.0025 N. The decomposition in 0.0006 N salt is detectable after 2 hours. A visible

FIG. 2A
Catalysis by ferric sulph. at diff. pH.

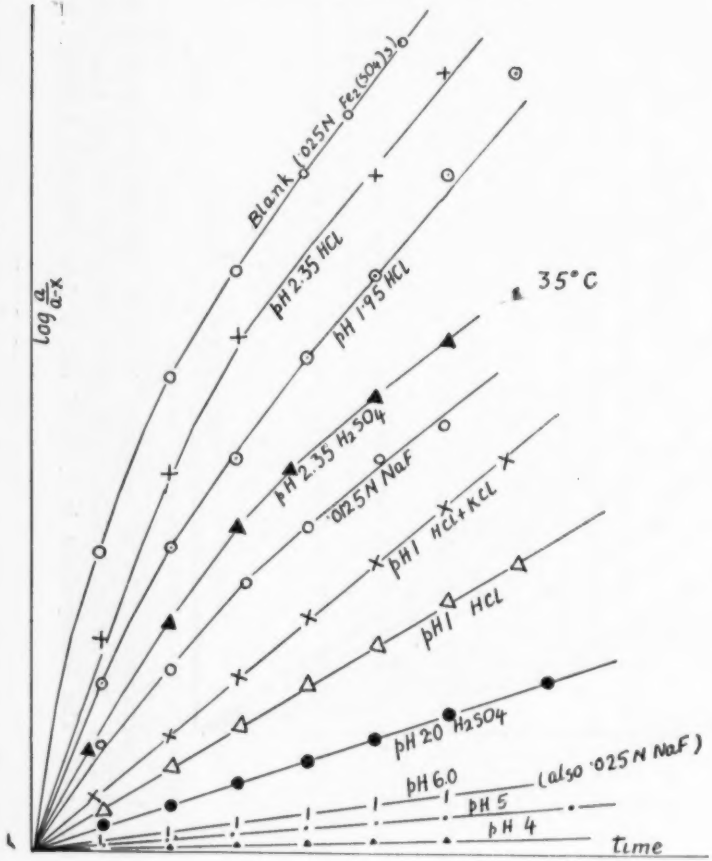
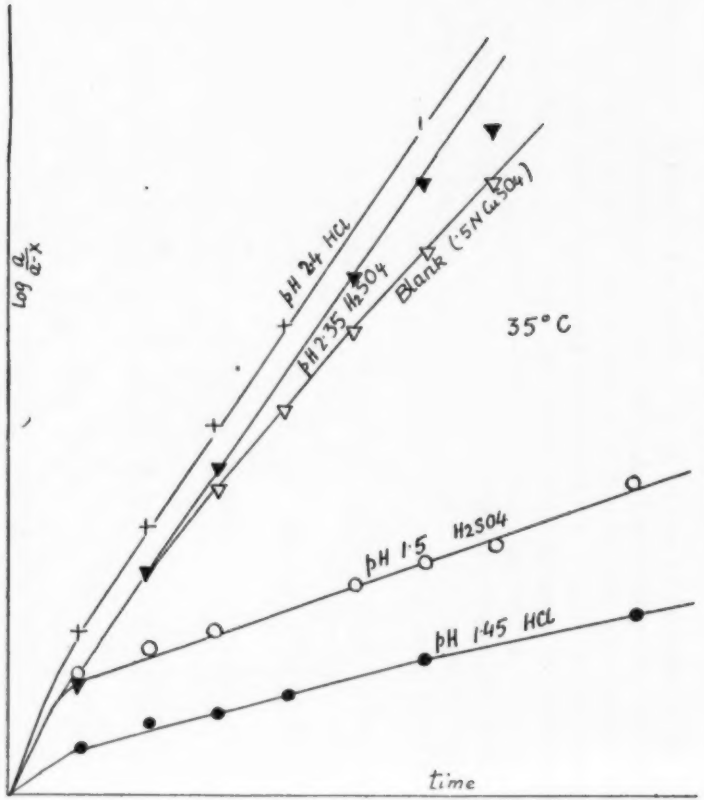


FIG. 2B
Catalysis by Copper sulph. at diff. pH.



hydrolysis of the salt takes place at 0.005 *N*. The oxide formed is finer as the concentration of the salt is decreased, and the time required for settling of the precipitate is increased from 20 to 80 minutes as the concentration is decreased to 0.0012 *N*. The loss of activity consequent upon the decrease of free ferric ions is remarkable. We realised in this work that the p_H in the various mixtures could not be the same. To see the effect of p_H, we selected the mixture in which the iron salt was 0.025 *N*. Suitable buffer mixtures were added in such volumes that after final dilution with distilled water, the solution had p_H 1, 2, 3 ..... 6. The first three involved KCl-HCl mixtures, while the last three were adjusted with sodium acetate - acetic acid mixtures. The results are shown in Fig. 2A. It appears curious at first sight that the rate increases at first with increasing p_H, but a reversal sets in at p_H 3. However, in sodium acetate- acetic acid mixtures, there is the possibility of removal of ferric ions by complex formation, which again supports the view that the free Fe^{3+} is the catalyst. One should expect that progressive addition of sodium fluoride should likewise produce a corresponding depression in the catalytic activity. This is actually seen in Fig. 2A. Subsequently, we adjusted the p_H of the mixture by known amounts of HCl or H_2SO_4. Instead of calculating the p_H, we measured it on a Beckman p_H meter and found a uniform increase in the decomposition rate with the increase in p_H. The p_H of the practically neutral ferric sulphate was 2.35 to 2.40; so it was not possible to adjust the value at a higher figure by decreasing the amount of acid. The same appears to be true of 0.5*N*-$CuSO_4$. Although the presence of a small amount of acid does not affect appreciably the p_H of the neutral ferric sulphate, it unexpectedly produces an improvement on the value of k, perhaps by suppressing the rate of hydrolysis, unless the increase represents a salt effect (Fig. 2B).

TABLE I

Ferric sulphate.			Copper sulphate.		
Acid.	p_H.	k.	Acid.	p_H.	k.
Nil	2.35	0.0284	HCl	1.45	0.00072
HCl	1.00	0.0061	HCl	2.40	0.00342
HCl	1.95	0.0189	H_2SO_4	1.50	0.00122
HCl	2.35	0.0316	H_2SO_4	2.35	0.00302
H_2SO_4	2.35	0.0156			
H_2SO_4	2.00	0.0034			

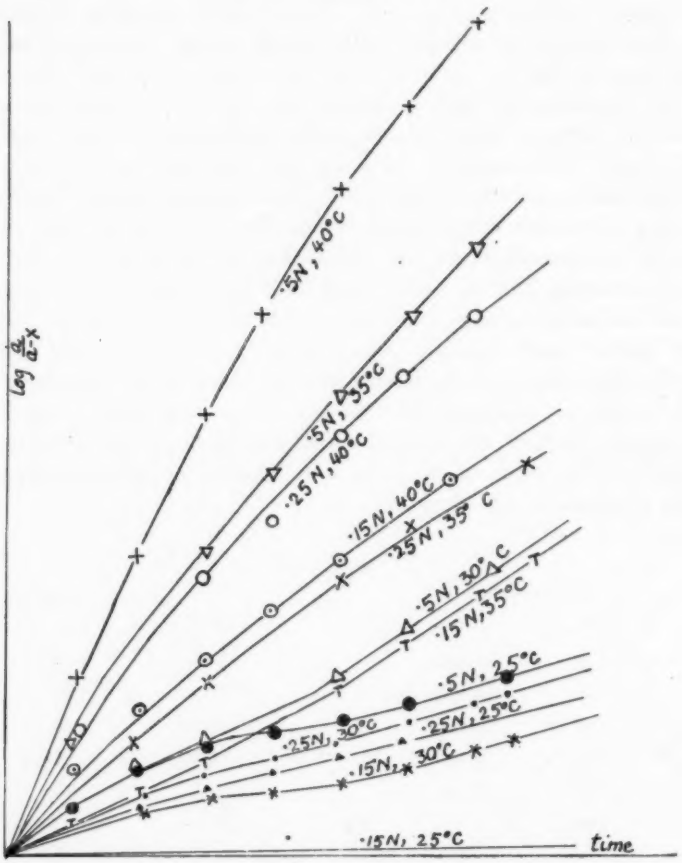
Catalysis by Cupric Sulphate and Ceric Ammonium Nitrate

Experiments with copper sulphate and ceric ammonium nitrate showed that the activity was much less even when enough of these salts was present (Fig. 3). In absence of acid, less than 10% of the peroxide was decomposed in the first 10 minutes and barely 20% in 120 minutes. 0.15*N*-$CuSO_4$ at 25° hardly showed any activity. The decomposition in presence of neutral ceric nitrate was somewhat better initially. When acid was added to these mixtures, there was a definite fall in the rate of decomposition (Fig. 2B). It is curious that HCl and H_2SO_4 do not produce identical results.

It will be seen that there is no sudden increase in the rate of decomposition as the concentration of Cu^{2+} is increased. This is natural since copper ions do not undergo extensive hydrolysis like iron ions. On the other hand, catalysis by Ce^{4+} is again curious. There is a large rate at the beginning which, we believe, is due to Ce^{4+} ions.

FIG. 3

Catalysis by $CuSO_4$ solns.



But hydrolysis soon sets in so that the subsequent rate is quite slow, which, we presume, is due to cerous oxide. Almost all the ceric ions were reduced to cerous since ceric nitrate in the concentration used did not produce any precipitate till peroxide was added. It is also well known that H_2O_2 may be quantitatively estimated with ceric salts (Vogel, "Quantitative Inorganic Analysis", p. 311, 1935, Longmans, Green & Co., London).

Catalysis by Potassium Iodide and Manganous Sulphate

The action of iodide ions in presence of increasing quantities of sulphuric acid was also studied. We prepared mixtures of 0.08*N*-H_2O_2 and 0.4*N*-KI. The total volume of oxygen evolved in 10 minutes was measured and converted to grams, the mixtures being maintained at 35°, with the following results.

TABLE II

Acid in mixture	Nil	*N*/1600	*N*/800	*N*/400	*N*/200	*N*/100
Oxygen (g.)	0.03064	0.03055	0.03051	0.03045	0.02948	0.02876

The total oxygen expected was 0.0320 g., so that when only small quantities of acid were present, the evolution was complete within a few per cent. But in *N*/100-acid, about 10% of the oxygen failed to appear. It appears therefore that the possibility of oxidation of iodide ions to iodine exists in such solutions:

$$2H_2O_2 + 2KI + H_2SO_4 \rightarrow 2H_2O + I_2 + K_2SO_4.$$

However, in earlier works iodide ion was considered to be oxidised in alkaline solutions by peroxide, the reaction being purely catalytic in neutral solutions (Bredig and Walton, *Z. Elektrochem.*, 1903, **9**, 114, quoted by Newton Friend, *loc. cit.*, p. 338). $V_2O_2Cl_4$ was found to be another good catalyst. A solution, which was 0.125 *N*-H_2O_2 and 0.0225 *M*-$V_2O_2Cl_4$, showed 67% loss of peroxide in 10 minutes.

Mixtures were also prepared containing 0.10*N*-H_2O_2 and increasing concentrations of manganous sulphate. The catalytic power increased with increasing concentration of the salt. The first order rate constants at 35° were found to be 0.00058 at 0.25 *M*, 0.0015 at 1.3 *M*, 0.0039 at 2.5 *M* and 0.0127 at 4 *M* salt. The graph of the velocity constant, k, against salt concentration is shaped like a rectangular hyperbola, showing that increase in the concentration of $MnSO_4$ beyond 4 *N* would not produce a further increase in k.

DISCUSSION

If a is the initial concentration of H_2O_2 and x, the amount decomposed at time t minutes, $\log a/(a-x) = kt$, if the reaction is of the first order. Figs. 1–3 show the plots of $\log a/(a-x)$ against time. The graphs are approximately straight lines in limited number of cases and deviate towards decreased values of k, when the concentration of H_2O_2 becomes small in any experiment due to the reaction.

No new substance accumulates in the system as the decomposition progresses. Whereas the concentration of a catalyst remains the same throughout, the ratio of catalyst to peroxide increases with the amount decomposed. It appears that a high ratio is not always favourable to the reaction. Reduction of the catalyst to a lower state of oxidation is likely to be small, but perhaps the ratio of the oxidised state to the reduced state may change in favour of the latter as the concentration of peroxide is decreased. This will affect the rates of (b') and (c'), and perhaps the overall rate of decomposition. It may be noted that the initial ratio of peroxide to catalyst in our experiments varies from 0.6 to 600 for iron, from 0.4 to 1.34 for copper, from

0.25 to 4 for manganese, and 10 to 160 for iodide. In spite of the remarks made above, we failed to detect any iodine by ordinary methods. It is doubtful therefore whether in other cases also the oxidation state is changed to any large extent. It is remarkable that in spite of such large variations in the peroxide : catalyst ratio, the apparent first order k should be so substantially constant in some cases.

The experiments with ferric and copper sulphates were repeated at other temperatures also, and the apparent energy of activation calculated from the changing k, with the following results.

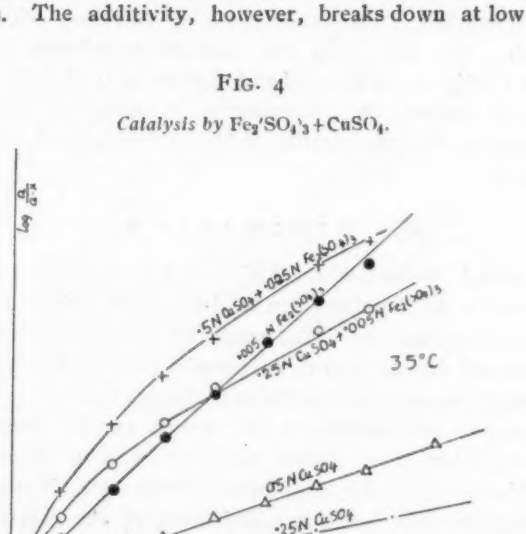
TABLE III

Conc. of ferric sulphate	...	0.025 N	0.05 N	0.075 N
Energy, E (cal./mole)	...	13300	13100	12900
Conc. of copper sulphate	...	0.15 N	0.25 N	0.50 N
Energy, E (cal./mole)	...	19000	18900	18900

The apparent energy of activation in presence of copper ions is appreciably higher than that in presence of ferric ions. If the mechanism of reaction with copper ions is substantially similar to ferric ions, discussed in the beginning, the actions in mixed solutions are likely to be additive. This was satisfactorily borne out from some of our experiments in which the mixture was made 0.1 N-H_2O_2, 0.025 N-ferric sulphate and 0.5 N-copper sulphate. When the rates for the two salts are separately calculated for hydrogen peroxide left at the moment (obtained from two separate experiments, one for iron and the other for copper ions), the overall rate agrees with the sum of the calculated rates. The additivity, however, breaks down at low concentrations of H_2O_2 (Fig. 4).

FIG. 4

Catalysis by $Fe_2'SO_4'_3 + CuSO_4$.



It seems that the simple mechanism, outlined above, is sufficient to explain the general observations. Fe^{3+} may be changed by any other ion which can readily change

its state of oxidation. We tried a number of salts in moderate concentrations which do not possess this property, viz., $MgSO_4$, $MgCl_2$, $CaCl_2$, $ZnSO_4$, $NiCl_2$, $NiSO_4$, NaCl, KCl and Na_2SO_4, but in none of these cases did we observe any catalytic effect. The adverse effect of H^+ ions on the decomposition is clearly seen (Eq. *a*) and the fundamental similarity between the actions of Fe^{3+} and Fe^{2+} ions is understood. Introduction of OH^- ions would shift the equilibrium in (*a*) to the right, providing a large concentration of O_2^{2-}, and oxygen may be liberated according to (*b'*) even if a trace of catalyst is present in preference to (*b*), which would be to a certain extent depressed by large concentrations of OH^- ions. According to this mechanism, relatively high concentrated solutions of hydrogen peroxide may be more stable in complete absence of a catalyst, as is well known (Mellor, *loc. cit.*).

On the other hand, Haber and Weiss (*loc. cit.*) and Barb *et al.* (*loc. cit.*) insist that the mechanism involves the production of free radicals (OH, HO_2) and subsequent setting up of reaction chains. One of the evidences pointed out by Barb *et al.* is that H_2O_2, catalysed by an iron salt, can initiate polymerisation, e.g., of acrylonitrite, such polymerisation being characteristic of free radicals. However, by suitable choice of concentrations there is no polymerisation at all. Haber and Weiss (*loc. cit.*) refer to the phenomenon of 'Katalasestoss', observed by Kuhn and Wassermann (*Annalen*, 1933, **503**, 203). Obviously, the explanation given by Haber and Weiss for the abnormal increase in rate of decomposition is far from simple. The conditions suggested by them are : (*i*) a high concentration of H_2O_2 ; (*ii*) a low concentration of Fe^{3+} such as may be existing in ferric acetate or succinate ; (*iii*) an Fe^{2+} remover, e.g. $\gamma\gamma'$-dipyridyl. When these external materials are introduced into the system, it is doubtful whether their action can be regarded as merely adjusting the concentrations concerned. At low concentrations (e.g. 0.05 *M*) $FeCl_3$ is likely to hydrolyse quickly (Gyani *et al.*, *loc. cit.*). It appears to us that an important aspect concerning the state of catalysing ions has been ignored in these discussions. It appears quite likely that ion pairs, triplets, etc. may exist in solutions when conditions are appropriate. It is also likely that interionic distances in these pairs may change with concentration, ionic strength and other conditions, and it may be only with selected values of these distances and configurations that catalysis may be favoured. It does not appear justified that Balandin's views concerning catalysis by solids (*Z. physikal. Chem.*, 1929, **B2**, 289) should be completely ignored for solutions. 'Katalasestoss' may well be explained on the basis of such favoured conditions existing in particular mixtures.

In any case, there is no denying that even for solutions there is a good deal of specificity observed. Indeed, some old observations on the catalytic decomposition of H_2O_2 are remarkable. Thus, finely divided platinum, manganese dioxide and charcoal powder are catalysts and perhaps to a lesser extent so are finely divided iron and copper, cerium and manganese in neutral solutions. Among oxides of copper, cerium, manganese and iron, the best is MnO_2 followed by CuO, CeO_2 and Fe_2O_3. This is precisely the reverse order for the corresponding cations in solution, Fe^{3+}, Cu^{2+} and Mn^{2+}. We find from our preliminary work that the activity of an oxide decreases as the water content is decreased by heating at increasing temperatures, which is likely

to affect lattice dimensions of the solids. It appears that a larger stress on physical conditions of catalysts, both in the solid state and in solutions, is necessary and little purpose is served in analysing data from a limited number of experiments. Even Haber and Weiss appear to realise this situation (*loc. cit.*, p. 348).

The falling off of the first order velocity constant at lower concentrations of H_2O_2 recalls the similar observation with homogeneous gas reactions. The well-known explanation in the latter case due to Lindemann (*Trans. Faraday Soc.*, 1922, **17**, 598) is that in the first place activated molecules of the reactants are formed, but not all of them decompose to yield the desired products. If most of them revert to the unactivated condition before reaction takes place, the process, which may be bimolecular as to the activation process, may appear as unimolecular as to decomposition. Since deactivation would be less frequent at low pressures, if a stationary state is attained, the rate of reaction would approach the rate of activation so that the order would tend to be 2, and a fall in the first order rate constant would be observed if an attempt is made to set down the data in accordance with such a process. The presence of water molecules in the reaction mixture offsets a simple explanation of the falling k on these lines, but the situation still points out that the H_2O_2 molecules may be in an activated condition in reaction (c').

It appears therefore that the energies of activation, we have determined above, correspond to the activation of H_2O_2 molecules, and the chief function of a catalyst may be to lower this value. In such a case, one may look out for an association of the catalysing ion with the peroxide molecule, resulting in the formation of a charged complex. We should then expect salt effects. This matter is receiving our attention. We may add that we have secured definite evidence of such effects in the heterogeneous catalysis in presence of CuO.

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RUBEANIC ACID AND ITS DERIVATIVES AS COLORIMETRIC REAGENTS PART II. DIMETHYL - AND DIETHYL- RUBEANIC ACIDS

By J. Xavier and Priyadaranjan Rây

NN'-Dimethyl- and -diethyl-rubeanic acids react in a similar manner as rubeanic acid, furnishing coloured precipitates with solutions of salts of various metals like, Pd, Au, Ag, etc. The solubilities of these metal complexes also closely follow those of rubeanates. Spot tests of Cu, Co, Ni and Pd show identification limits comparable to those of the parent compound. Spectrophotometric determinations of the above metals, excluding copper, have also been made as in the case of rubeanic acid.

The use of rubeanic acid in the spectrophotometric determination of cobalt, nickel, palladium, silver and ruthenium has been reported earlier (this *Journal*, 1958, **35**, 432). The introduction of certain radicals into organic reagents, containing certain reactive groups, has been found to exert an influence on the solubility of the reagent, on its ability to form salts and on the solubility characteristics of its reaction products. The influence of weighting and/or size effect is considered to be mainly responsible for such a behaviour. A comparative study of certain disubstituted rubeanic acids was therefore deemed desirable with a view to examining the influence of substitution on their properties as analytical reagents (Xavier and Rây, *Science & Culture*, 1954, **21**, 694).

Experimental

The *NN'*- dialkyl substituted rubeanic acids were obtained by warming rubeanic acid with the corresponding primary amines in alcohol (Wallach and Reinhardt, *Annalen*, 1891, **262**, 354; Woodburn and Sroog, *J. Org. Chem.*, 1952, **17**, 376).

Dimethyl rubeanic acid (CH_3-NH-CS-CS-NH-CH_3) and diethylrubeanic acid (C_2H_5-NH-CS-CS-NH-C_2H_5) behave in a manner almost similar to rubeanic acid (Feigl and Badian, unpublished work ; cf. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions", p. 44, Academic Press, New York, 1949). Like rubeanic acid they give coloured precipitates with solutions of salts of various metals like copper, cobalt, nickel, palladium, silver, gold, platinum, lead, mercury, etc. The characteristic properties of these precipitaties are summarised in Table I.

TABLE I

Metals.	(I) Dimethylrubeanic acid.	(II) Diethylrubeanic acid.
Copper	Deep green ppt. with a faint blue tinge from ammoniacal, neutral or weakly acid (acetic) solns. Almost insoluble in dil. acids, alkalies and in all the common solvents.	Green ppt. with a blue tinge. Same as I.
Cobalt	Deep brown ppt. in ammoniacal medium. Insoluble in dil. acids and alkalies. Fairly soluble in pyridine (orange-yellow soln.), extractable by *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate and chloroform).	Same as I. The pyridine soln. is extractable also by benzene and toluene.
Nickel	Reddish violet ppt. in ammoniacal medium. Insoluble in dil. acids or alkalies. Easily soluble in pyridine (reddish pink solution extractable by common solvents).	Deep purple-red ppt. in ammoniacal medium. Solubility same as I. The pyridine soln. is pink-red.
Palladium	Orange-yellow ppt. in very dil. acid medium. Slightly soluble in dil. acids and decomposed by dil. alkalies. Soluble in most of the solvents. Pyridine soln. is coloured orange-yellow.	Same as I.
Silver	Orange-yellow ppt. from neutral soln. decomposed by dil. acids or alkalies.	Deep orange-yellow ppt. in neutral soln., same as I.
Gold	Yellowish white ppt. from dil. acid soln., decomposed on standing.	Orange-yellow ppt., same as I.
Platinum	Pale yellow ppt. from acid soln., turning orange-yellow on standing.	Orange-brown ppt.
Lead	Voluminous yellow ppt. from neutral or alkaline soln., decomposed by dil. acids.	Yellow ppt., behaves as I.
Mercury (II)	White ppt. from neutral soln., stable towards dil. ammonia or alkali solns., decomposed by dil. acids.	Same as I.

Manganese, chrominum, titanium, tin, molybdenum, tungsten, vanadium, zinc, cadmium, uranium, arsenic, antimony, etc. do not react with these reagents. Ruthenium gives a coloured solution (blue) in acid medium as with rubeanic acid.

Spot Test Detections.—Cu, Co, Ni and Pd can be detected by the spot-tests. The following procedure was adopted. A drop of the sample solution was placed in the depression of the spot plate, followed by another drop of very dilute ammonia. One drop of the reagent solution (0.1% alcoholic) was placed very near to the first drop. As the drops mixed together, characteristic colours or precipitates were observed on the boundary zone. Copper is identified by its light green precipitate, cobalt by yellowish brown colour or precipitate and nickel by pink colour or precipitate. Palladium is detected by the yellow colour, produced in a similar way, but without adding ammonia solution. The formation of characteristic colours took about 3 to 5 minutes after the drops got mixed. For comparison, a blank was also carried out. The following identification and concen-

tration limits were obtained: Cu, 0.18γ (1:2.3 × 10⁵); Ni, 0.04γ (1:1.25 × 10⁶); Co, 0.025γ (1:2 × 10⁶); Pd, 0.067γ (1 : 5 × 10⁵).

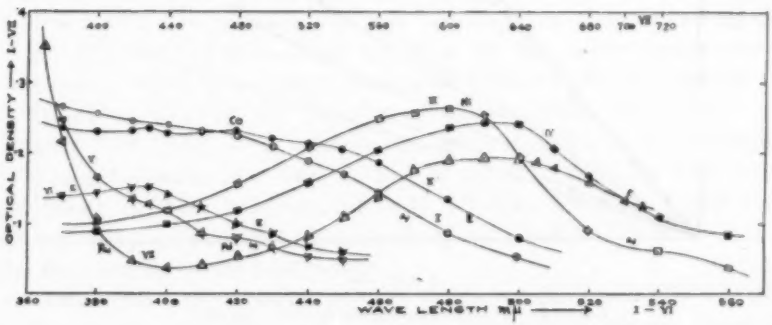
Spectrophotometric Determinations.—Co, Ni and Pd have been spectrophotometrically determined in aqueous pyridine solution, using alcoholic-sodium hydroxide solutions of dimethyl- and diethylrubeanic acids. Copper, however, could not be determined in this way due to the low solubility of the copper rubeanate in pyridine solution. The determination of ruthenium was carried out in strong hydrochloric acid solution, using an alcoholic solution of the reagent. The sensitivities of the cobalt and palladium reactions are almost the same as those with rubeanic acid, while nickel and ruthenium estimations give slightly higher values. The colour development was retarded by excess of alkali, when the diethyl derivative was employed for the determinations.

Determination of Cobalt

Cobalt developed an orange-yellow colour in aqueous pyridine with an alcoholic sodium hydroxide solution of diethyl- or dimethyl- rubeanic acid. The colour development was rapid in presence of sodium acetate, although for higher concentrations of cobalt (>3 p.p.m.) 30 to 45 minutes were required to reach the maximum intensity. The optical density thereafter remained unaltered for more than 24 hours at the room temperature. A Unicam SP 600 spectrophotometer was used for the measurement.

FIG. 1

Absorption curves.



Curve I —1 p.p.m Co; 5 c.c. pyridine; 2 c.c. dimethylrubeanic acid reagent soln. and 1 c.c. sodium acetate soln. in 25 c.c. final volume.

Curve II —Same as for I; 1 c.c. diethylrubeanic acid reagent soln.

Curve III—2 p.p.m. Ni; 5 c.c. pyridine; 2 c.c. dimethylrubeanic acid reagent soln. in final volume 25 c.c.

Curve IV —Same as III; 1 c.c. diethylrubeanic acid reagent soln.

Curve V —2 p.p.m. Pd; 5 c.c. pyridine; 1 c.c. dimethylrubeanic acid reagent soln. in final volume 25 c.c.

Curve VI —Same as for V; 1 c.c. diethylrubeanic acid reagent soln.

Curve VII—2 p.p.m. Ru; 1 c.c. of reagent (dimethyl or diethylrubeanic acid) soln. in final volume 25 c.c.

Standard cobalt solution contained 1γ Co/c.c. Reagent solution was prepared by mixing equal volumes of 0.1% alcoholic solution of dimethyl- or diethyl- rubeanic acid and $N/4$ aqueous NaOH solution. In presence of NaOH, dimethyl- or diethyl-rubeanic acid solution was coloured faintly yellow. 1% Aqueous sodium acetate was used.

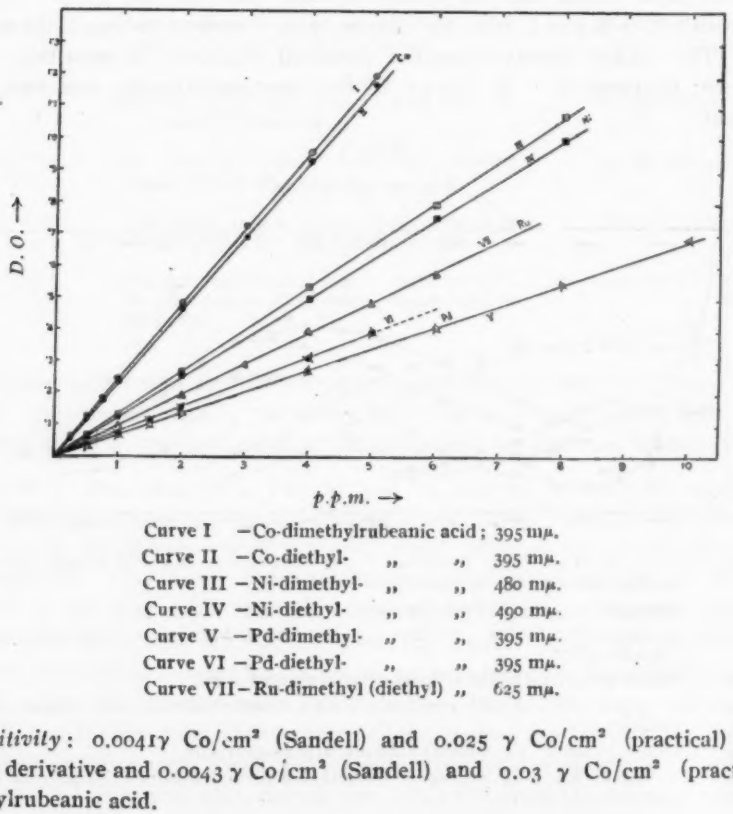
Absorption Curves.—Against a reagent blank, the orange-yellow colour of the test solution gave constant absorption in the region 385-395 mμ (cf. Curves I & II, Fig. 1). Measurements of optical density were made at 395 mμ where the absorption of the reagent solution was comparatively small.

Effect of NaOH *Concentration.*—The maximum permissible concentration of the alkali was found to be 0.04 to 0.05 N in the total volume, beyond which the optical density diminished.

Beer's Law.—Curves I and II, Fig. 2 show the linear relationship between the metal concentration and optical density, measured 30-45 minutes after preparing the solutions.

FIG. 2

Beer's law curves.



Curve I —Co-dimethylrubeanic acid; 395 mμ.
Curve II —Co-diethyl- ,, ,, 395 mμ.
Curve III —Ni-dimethyl- ,, ,, 480 mμ.
Curve IV —Ni-diethyl- ,, ,, 490 mμ.
Curve V —Pd-dimethyl- ,, ,, 395 mμ.
Curve VI —Pd-diethyl- ,, ,, 395 mμ.
Curve VII—Ru-dimethyl (diethyl) ,, 625 mμ.

Sensitivity: 0.0041γ Co/cm² (Sandell) and 0.025 γ Co/cm² (practical) for the dimethyl derivative and 0.0043 γ Co/cm² (Sandell) and 0.03 γ Co/cm² (practical) for the diethylrubeanic acid.

Effect of Diverse Ions.—The following ions interfered as they either formed precipitates or coloured solution on the addition of the reagent: Fe^{3+}, Fe^{2+}, Bi^{3+}, Hg^{2+}, Mn^{2+}, Ag^{+}, Au^{3+}, Pt^{4+}, Pd^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, VO_3^{-}, etc. The use of potassium cyanide to mask the colour effect due to nickel may be made as in the the case of rubeanic acid (cf. Part I, *loc. cit.*).

Procedure.—Sodium acetate (1 c.c.) and pyridine (5 c.c.) were added to an almost neutral solution of cobalt, containing less than 0.1 mg. Co. About 10-15 c.c. of water was added, followed by 2 c.c. of the reagent solution. The volume was made up to 25 c.c. with water and the optical density measured at 395 mμ, after 30-45 minutes, against a suitable reagent blank.

Determination of Nickel

With very dilute nickel solutions in presence of pyridine, dimethylrubeanic acid developed a purple-yellow colour, and the diethyl derivative, a rose-red solution. With low concentrations of nickel, the colour development was retarded by excess of alkali in the case of diethylrubeanic acid. The colour systems obeyed Beer's law.

Standard nickel solution contained 2.5 γ Ni/c.c. Reagent solution comprised equal volumes of 0.2% alcoholic solution of dimethyl- or diethyl-rubeanic acid and $N/4$ aqueous NaOH solution.

Absorption Curves.—The absorption maximum for the purple-yellow colour of nickel dimethylrubeanic acid was found to lie at 485 mμ and that for the rose-red colour of nickel diethylrubeanic acid at 490 mμ (cf. Curves III and IV, Fig. 1). All optical density measurements were made against a reagent blank, which showed only a negligible absorption beyond the ultraviolet region.

Effect of NaOH *Concentration.*—It was observed that dilute alkali solutions (up to 10 c.c. of $N/4$) for 2 γ Ni/c.c. had no effect on the colour intensity of nickel dimethylrubeanate, when added after the reagent solution. But the addition of alkali to the diethyl system retarded the colour development. Thus, when 1 c.c. of $N/4$-NaOH solution was added to a solution containing 2 p.p.m. Ni, 5 c.c. pyridine and 2 c.c. of the reagent solution in a total volume of 25 c.c, made up with water, the maximum colour intensity was reached only after 30 minutes. Under the same conditions, but with 2 c.c. of alkali, it took about 1½ hours, and with 10 c.c., about 3 hours for the complete colour development.

Beer's Law.—Both the systems followed Beer's law (cf. Curves III & IV, Fig. 2). When diethylrubeanic acid was used as the reagent, optical density measurements were taken after a lapse of 30 minutes from the time of preparing the solutions.

Stability of the Colour.—The purple-yellow colour of the nickel dimethylrubeanate developed within 15 minutes after the addition of the reagent, and was stable for about 3-5 hours. The optical density of the coloured system in the case of diethylrubeanic acid remained unchanged for about an hour, but increased slowly by 8-10% after 12 hours.

Sensitivity: 0.0075γNi/cm² (S) and 0.03γNi/cm² (P) for dimethylrubeanic acid. 0.008 γ Ni/cm² (S) and 0.03 γ Ni/cm² (P) for diethylrubeanic acid.

Effect of Diverse Ions: Same as under cobalt.

Procedure.—Pyridine (5 c.c.) and water (10 c.c.) were added to the sample solution, which was previously made almost neutral. The reagent solution (2 c.c., for dimethyl- and 1 c.c. for diethyl-rubeanic acid) was added and the volume made up to 25 c.c. with water. The optical density was measured against a reagent blank after 10 minutes for dimethyl- and after 30 minutes for diethyl-rubeanic acid.

Determination of Palladium

The yellow colour developed by the addition of dimethyl- or diethyl-rubeanic acid reagent solution (vide under Ni) to an aqueous pyridine solution of palladium gave decreasing values of absorption at higher wave-lengths (cf. Curves V & VI, Fig. 1). 395 mμ was found to be the most desirable wave-length, at which the reagent absorption was quite small. Addition of an excess of alkali was found to retard the colour formation. Thus, 1 c.c. of $N/4$-NaOH, added 3-5 minutes after the reagent, diminished the optical density of a solution containing 2 p.p.m. Pd by about 5% when measured at 395 mμ, after half an hour. The colour development was rather slow at higher concentrations (>4 p.p.m.) of palladium, taking about 20 to 30 minutes to reach the maximum intensity. But the intensity afterwards remained unchanged for more than 24 hours. The systems were found to obey Beer's law (cf. Curves V & VI, Fig. 2).

Sensitivity: 0.014 γ Pd/cm² (S) and 0.05 γ Pd/cm² (P) for dimethylrubeanic acid. 0.013 γ Pd/cm² (S) and 0.05 γ Pd/cm² (P) for diethylrubeanic acid.

Procedure.—Same as that for nickel. But 1 c.c. of the reagent solution was used, and the optical density was measured at 395 mμ, about half an hour after preparing the solution.

Determination of Ruthenium

The procedure adopted was similar to that for rubeanic acid. Ruthenium solutions, when warmed with dimethyl- or diethylrubeanic acid in presence of HCl, developed a blue colour. The absorption maximum of this solution lay in the region of 600-640 mμ for dimethyl- and 610-660 mμ for diethyl-rubeanic acid (cf. Curve VII, Fig. 1). 625 mμ was chosen for the analytical work.

HCl-EtOH mixture (2.5 c.c., 1:1 by vol.) and 0.2% alcoholic reagent solution (1 c.c.) were sufficient to develop the maximum colour intensity. But when the ruthenium content was more than 5 p.p.m., an excess of the reagent as well as of the acid-alcohol mixture were necessary. Beer's law was found to hold good up to 4 p.p.m. Ru for dimethyl and up to 6 p.p.m. for the diethyl derivative (Curve VII, Fig. 2). Both the reagents gave the same sensitivity of 0.01 γ Ru/cm² (S) and 0.04 γ Ru/cm² (P).

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COMPLEX COMPOUNDS OF MANGANESE (III) WITH BIGUANIDES

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Some stable cationic chelate complexes of tripositive manganese with biguanide and ethylenedibiguanide have been isolated and studied. A particularly interesting feature of these complexes is indicated by the fact that in them the manganese atom is co-ordinated with nitrogen atoms of the ligand molecules, instance of which is not found in the literature as yet. Furthermore, barring the single instance of *bis*-acetylacetone- diaquo manganese (III), the compound described in this paper represent the only well-defined series of some cationic complexes of tripositive manganese.

$[(OH)(H_2O)\ Mn^{III}\ (Big)_2]$ (where Big H is a molecule of biguanide), presumed to be the initial product of reaction, forms in vacuum a diol binuclear complex of the type (I).

The latter becomes anhydrous at 90° without any decomposition. Its effective moment value of 4.7 μ_B suggests the presence of outer-level sp^3d^2 hybrid bonds or ion-dipole bonds. The ethylenedibiguanide complex, $[(OH)(H_2O)\ Mn^{III}\ Et\ (Big)_2]$, which forms dark chocolate-red crystals, is stable even up to 110°. In view of its low moment value of 3.26 μ_B, it may be regarded as a penetration complex with d^2sp^3 bonds with some imperfectly quenched orbital moment. In faintly acid solutions, a diaquo complex cation is formed, which has been isolated as a series of its salts having the composition, $[(H_2O)_2\ Mn^{III}Et(BigH)_2]X_3$, where $X = \frac{1}{2}(SO_4)$, $\frac{1}{2}(SeO_4)$ and $\frac{1}{2}(CrO_4)$. They form yellow to yellowish brown silky crystals. These, however, show effective moment values of 4.58 μ_B, characteristic of Mn^{3+} ion. These salts therefore represent associated or outer-level complexes with sp^3d^2 hybrid bonds resonating with ionic ones. Both the hydroxo-aquo and diaquo complexes possess presumably the *trans*-structure in view of the fact that the quadridentate ethylenedibiguanide ligand tends preferably to assume a planar orientation around the central metal atom.

Biguanide and its substituted derivatives have been shown by Rây and co-workers (this *Journal*) to possess remarkable capacity for co-ordination with transitional metal atoms, giving rise to extraordinarily stable inner-level or penetration complexes. Previous investigations were concerned mainly with Cu^{II}, Ni^{II}, Co^{II}, Pd^{II}, Co^{III}, Cr^{III} and Ag^{III}. The silver ethylenedibiguanide serves indeed as a unique instance of a cationic complex of the metal in the tripositive state. The present investigation deals with a study of the preparation and properties of some similar stable cationic complexes of biguanide and ethylenedibiguanide with tri- and tetrapositive manganese.

Tervalent manganese, owing partly to its comparatively high electronegativity, has a more or less pronounced tendency to form complexes in which its valency stage is stabilised. The electronic configuration of the manganic ion, with four $3d$ electrons is, on the basis of Pauling's theory, also favourable for the formation of hybrid covalent bonds. That so far only a few such complexes have been prepared, might be ascribed to the ease with which the Mn^{3+} ion hydrolyses with the precipitation of Mn_2O_3 or its hydrates.

Tripositive manganese mostly forms complexes of the ionic type with ligands of high electronegativity containing oxygen as the donor atom, such as, oxalic acid, malonic acid, salicylic acid, sulphuric acid, phosphoric acid and iodic acid.

Complex fluoride, chloride and cyanide are also fairly known. Like many other tripositive ions, Mn^{III} forms neutral complexes with acetylacetone and benzoylacetone. The cationic complexes of tripositive manganese are on the other hand relatively scarce. The only instance of the type, reported lately, is furnished by *bis*-acetylacetone-diaquo manganese^{III} salts isolated by Cartledge (*J. Amer. Chem. Soc.*, 1952, **74**, 6015) as the olive-green perchlorate and chloride. Moreover, manganese has been found to show little tendency to co-ordinate with nitrogen atom as donor.

It is therefore significant that manganese has been found to give rise to stable cationic chelate complexes in its tri- and tetrapositive states by co-ordinating with the nitrogen atoms of the biguanide ligands. An account of the preparation and properties of the tripositive complexes with biguanide and ethylenedibiguanide is given in the present paper. Those of the tetrapositive metal with the same ligands have been reported in a separate communication in this issue.

The complex manganese (III) biguanide has been prepared by the aerial oxidation of a mixture of an excess of biguanide sulphate and manganous sulphate in strongly alkaline medium. The same compound is also formed on treating freshly prepared manganic acetate with an alkaline solution of biguanide. It forms dark chocolate-coloured shining crystals, insoluble in water. The vacuum-dried sample corresponds to the composition, $[(Big)_2\ Mn^{III}\ OH].0.5\ H_2O$, where BigH is a molecule of biguanide. It is presumed that $[(OH)(H_2O)Mn^{III}(Big)_2]$ or its hydrate is the initial product of reaction, which in vacuum loses water, giving rise to a diol binuclear compound of the type (I).

$$\left[\ (Big)_2\ Mn^{III}\begin{matrix}\nearrow OH \\ \nwarrow OH\end{matrix}Mn^{III}\ (Big)_2\ \right]\ .\ H_2O$$

(I)

At 90° the corresponding anhydrous compound is formed.

The complex manganese^{III} ethylenedibiguanide, $[(OH)(H_2O)Mn^{III}Et(Big)_2]$, where Et $(BigH)_2$ is a molecule of ethylenedibiguanide, has been prepared by the aerial oxidation of a mixture of ethylenedibiguanide sulphate and manganous sulphate in a strongly alkaline medium. It forms very stable dark chocolate-red crystals, sparingly soluble in water. The vacuum-dried sample, having the compsition $[(OH)(H_2O)\ Mn^{III}\ Et\ (Big)_2].\ 0.5\ H_2O$ loses 0.5 H_2O at 90°. In aqueous solution it suffers hydrolysis with the formation of a diaquo complex in equilibrium. The hydrolytic reaction is favoured by the presence of hydrogen ions, as is evident from the following representation :

$$[(OH)(H_2O)\ Mn^{III}\ Et(BigH)_2]^{2+} + H_2O \rightleftharpoons [(H_2O)_2\ Mn^{III}\ Et(BigH)_2]^{3+} + OH^-.$$

A series of complex diaquo salts of the composition: $[(H_2O)_2\ Mn^{III}\ Et(BigH)_2]X_3$, where $X = \frac{1}{2}(SO_4)$, $\frac{1}{2}(SeO_4)$ and $\frac{1}{2}(CrO_4)$, has been isolated from the solution of the hydroxo-aquo base in acetic acid by the addition of the corresponding alkali salts.

These form yellow or yellowish brown silky crystals, almost insoluble in water. Both the hydroxo-aquo and the diaquo complexes possess presumably the *trans* structure in view of the fact that the quadridentate ethylenedibiguanide ligand tends preferably to give rise to a planar configuration around the central metal atom.

The effective magnetic moment values of these tripositive manganese biguanide complexes, as determined from their susceptibility measurements, are shown in Table I.

TABLE I

Substance.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	* $D \times 10^6$.	$\chi_M \times 10^6$. (corr.)	μ_B. (effec.)
1. Diol-dimanganese *tetrakis*-biguanide	31 9	8963.9	+95 5	9059 4	4.70 (30°)
2. Hydroxo-aquo manganese ethylene-dibiguanide	12.68	4216.0	+132.2	4348.2	3 26 (30°)
3. Diaquo manganese ethylenedibiguanide sulphate	16.12	8333.0	+229.7	8562.7	4.57 (29 2°)
4. Diaquo manganese ethylenedibiguanide selenate	14.16	8320.0	+246.8	8566.8	4.58 (30°)

* D = diamagnetic correction.

It will be found that the compounds No. 1, 3 and 4 give moment values (4.6-4.7) more or less in agreement with the theoretical value of 4.9 μ_B on the basis of spin-only effective formula for the associated or outer-level complexes of tripositive manganese with no electron pairing. On the other hand, the compound No. 2, hydroxo-aquo manganese^{III} ethylededibiguanide, shows a much lower moment value of 3.26 μ_B, but somewhat higher than 2.82 μ_B, expected theoretically for a penetration or lower-level Mn^{III} complex in which electron pairing occurs with d^2sp^3 octahedral bonds. The difference might be attributed to the imperfect quenching of the orbital moment, contribution of which cannot therefore be altogether neglected (cf. Kotani, *J. Phys. Soc. Japan*, 1945, **1**, 293).

EXPERIMENTAL

Diol-di-Manganese^{III} tetrakis-*Biguanide Monohydrate*.—Biguanide acid sulphate (7 g.), dissolved in 8% NaOH solution (50 c.c.), was filtered by suction into a filter-flask, and to it a solution of $MnSO_4, 4H_2O$ (1 g. in 10 c.c. of water) was added with brisk shaking, when manganous hydroxide was precipitated. The filter-flask was closed with a bung, carrying an inlet tube reaching to the bottom of the flask, and a rapid current of air was drawn through the mixture for about 3 hours. The suspended manganous hydroxide was gradually converted into dark chocolate glistening crystals which accumulated at the bottom of the flask. After oxidation was completed (as indicated

by a clear orange-red supernatant liquid), the air current was stopped and the mixture was filtered by suction in a sintered glass crucible. The crystals on the filter-bed were washed several times with small portions of ice-cold water, sucked well and finally kept in vacuum over $CaCl_2$ and KOH ; yield 0.6-0.8 g.

The orange-red alkaline filtrate on being kept aside in air at room temperature deposited in a day or two shining red crystals analysing as $[(OH)_2Mn^{V}(BigH)_2](OH)_2$ (cf. this *issue*, p. 601).

The same tripositive manganese complex was also obtained by treating freshly prepared manganic acetate with an alkaline biguanide solution. Here also aerial oxidation led to the partial formation of the tetrapositive complex which remained in solution. [Found : Mn, 19.44 ; O(active), 2.83, 2.85 ; N, 50.67, 51.60. Formula of compound (I) requires Mn, 19.57 ; O(active), 2.85 ; N, 49.83%. Found (for the sample dehydrated at 90°) : O(active), 2.95. Calc. for the dehydrated product : O(active), 2.94%].

The product forms dark chocolate-coloured shining crysta's, insoluble in water. It loses its water of hydration at 90° without any decomposition and hydrolyses in contact with water, showing strongly alkaline reaction to litmus ($p_H>8$). It dissolves in dilute acetic acid to a brown solution which readily becomes turbid with precipitation of hydrated Mn_2O_3. A violet solution is obtained in syrupy phosphoric acid, characteristic of tripositive manganese compounds. A sample was found to remain unchanged when preserved for two months in vacuum over calcium chloride and caustic potash [O(active), 2.80%].

Hydroxo-aquo Manganese^{III} *Ethylenedibiguanide*.—Ethylenedibiguanide acid sulphate (5.4 g.), dissolved in 5% NaOH solution (60 c.c.), was filtered by suction into a filter-flask. It was then mixed with a solution of manganous sulphate (1.34 g. in 20 c.c. of water) when manganous hydroxide was precipitated. A brisk current of air was drawn through the mixture when the suspended manganous hydroxide gradually dissolved, giving a dark red solution. An almost clear solution was obtained within 15 to 20 minutes. Any insoluble matter was filtered off. A brisk current of air was passed through the filtrate again for about an hour in the cold. The crystals which separated were filtered by suction on a sintered glass-bed funnel, washed with ice-cold water and finally dried in vacuum over $CaCl_2$ and KOH ; yield 1.3-1.4 g. The dark red filtrate from above was kept aside for evaporation in air at room tepmerature, when a second crop of dark chocolate-red well-formed crystals separated from the solution. Unlike the case of simple biguanide, no further oxidation of tripositive manganese in the filtrate occurred here. {Found : Mn, 16.84 ; O(active), 2.46 ; N, 43.12. $[(OH)(H_2O)Mn^{III}Et(Big)_2].0.5H_2O$ requires Mn, 16.92 ; O(active), 2.46 ; N, 43.07%}.

The substance on being heated at 90° becomes anhydrous. [Found : O(active), 2.52. Calc. for the dehydrated product : O(active), 2.53%]. The compound suffered no further significant loss in weight when heated even up to 110°.

The substance forms dark chocolate-red crystals, sparingly soluble in water, giving a red solution. The aqueous solution is alkaline to litmus ($p_H > 8$) and is quite stable. Appreciable decomposition occurs only on prolonged boiling. In faintly acid solution it hydrolyses, forming a diaquo complex. It remains quite stable at room temperature for several months and gives a violet solution in syrupy phosphoric acid.

Diaquo Manganese^{III} Ethylenedibiguanidinium Sulphate.—A solution of hydroxo-aquo manganese^{III} ethylenedibiguanide (1 g. in 200 c.c. of cold water) was acidified with acetic acid and filtered. To the filtrate (p_H 4) was added a solution of ammonium sulphate (0.8 g. in 5 c.c. of water) dropwise with stirring. Yellow silky crystals separated in quantities. These were filtered by suction on a sintered glass-bed funnel, washed with cold water and dried in vacuum over $CaCl_2$. Finally the crystals were kept in air to acquire a constant weight; yield nearly quantitative. {Found: Mn, 10.61, 10.62; O(active), 1.54, 1.54; N, 27.26; SO_4, 27.66; H_2O (by loss at 70°), 10.33. $[(H_2O)_2Mn^{III}Et(BigH)_2](SO_4)_{1.5}.3H_2O$ requires Mn, 10.63; O(active), 1.55; N, 27 08; SO_4, 27.86; H_2O, 10.44%}.

The sample, when heated at 80° for 3 hours, lost 13.86% in weight (corresponding to loss of $4H_2O$). {Found (for the sample heated at 80°): O(active), 1.78; SO_4, 32.6. $[(H_2O)(SO_4)Mn^{III}Et(BigH)_2]\ (SO_4)_{0.5}$ requires O(active), 1.80; SO_4, 32.36%}.

The substance forms yellow silky crystals, almost insoluble in water. It becomes anhydrous at 70° and loses one molecule of co-ordinated water at 80° without any decomposition.

Diaquo Manganese^{III} Ethylenedibiguanidinium Selenate.—The complex selenate was prepared by adding dropwise a solution of sodium selenate to that of hydroxo-aquo manganese^{III} ethylenedibiguanide (1 g. in 200 c.c. of cold water), acidified with acetic acid. The yellow silky crystals that separated were filtered by suction on a sintered glass-bed funnel, washed with cold water and dried as usual; yield nearly quantitative. {Found: Mn, 9.41; Se, 19 97. $[(H_2O)_2Mn^{III}Et(BigH)_2](SeO_4)_{1.5}.3H_2O$ requires Mn, 9.35; Se, 20.16%}.

For the estimation of selenium, the complex was dissolved in 3*N*-HCl and heated on the water-bath with hydrazine sulphate. Metallic selenium separating was filtered, washed and dried to a constant weight at 120-30°. Manganese was estimated as $MnNH_4PO_4$, H_2O in the combined filtrate and washings.

The product forms yellow silky crystals, almost insoluble in water, and does not decompose even on boiling its aqueous suspension. It gives a violet solution in syrupy phosphoric acid as usual.

Diaquo Manganese^{III} Ethylenedibiguanidinium Chromate.—A solution of hydroxo-aquo manganese^{III} ethylenedibiguanide (1 g. in 200 c.c. of cold water) was treated with dilute acetic acid until the p_H was adjusted at 4.0. It was then filtered and the filtrate treated with a dilute solution of potassium chromate with stirring, when brownish yellow silky crystals separated out. These were filtered, washed and dried as

usual. {Found: O (active, total), 6.63. $[(H_2O)_2Mn^{III}Et(BigH)_2](CrO_4)_{1.5}.2.5H_2O$ requires O (active, total), 6.67%}. The product forms brownish yellow silky crystals, sparingly soluble in water.

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COMPLEX COMPOUNDS OF MANGANESE (IV) WITH BIGUANIDES

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Tetrapositive manganese has been found to form cationic complexes with biguanide ligands in which the nitrogen atoms function as donor atoms. These, we believe, represent the first cationic complexes of Mn^{IV} to be reported. $[(OH)_2\ Mn\ (BigH)_2]\ (OH)_2$ (where BigH is a molecule of biguanide) has been prepared in a variety of ways, e.g., by reduction of Mn^{VII} by ether and/or biguanide, and by oxidation of Mn^{II} with air, hydrogen peroxide or sodium persulphate. Starting from this complex base, a series of salts, namely, nitrate, sulphate, chromate, phosphate, oxalate, iodate and fluoberyllate, has been isolated and studied. Conductivity measurements in aqueous solution show that the complex nitrate dissociates as a bi-univalent salt with slight hydrolysis in dilute state. The valency of manganese in these complexes has been determined by oxidimetric titrations both against sodium thiosulphate (iodometry) and ferrous ammonium sulphate solutions. The corresponding dihydroxo manganese^{IV} ethylenedibiguanide base, $[(OH)_2\ Mn^{IV}\ Et(Big)_2].\ 1.5H_2O$, has also been prepared in a similar manner.

The unusually low magnetic moments (2.0–2.5 μ_B) of these complexes, an appreciable rise of the moment value of the complex nitrate in solution and a linear decrease in the effective Bohr magneton value of the solid nitrate from room temperature (300°K) down to 140°K indicate that they may be regarded as penetration or inner-level complexes with d^2sp^3 hybrid bonds with development of some antiferromagnetism, due possibly to metal-metal linkages in the solid state.

The tetrapositive manganese compounds with the single exception of MnO_2 are extremely unstable, at any rate in solution, partly because of the readiness with which they hydrolyse with precipitation of the insoluble manganese dioxide and partly because they are easily reduced by oxidisable substances present. They may, however, be stabilised by complex formation. With its much stronger electronegative character, tetrapositive manganese has relatively poor tendency to form complexes, and in fact, only a few of these like halogeno, cyano, iodato and oxalato complexes are described in the literature.

The halogeno complexes of Mn^{IV} are usually of octahedral type, M_2MnX_6. These are represented by the hexafluorides, M_2MnF_6 (Weinland and Lauestein, *Z. anorg. allgem. Chem.*, 1899, **20**, 40 ; Bellucci, *Atti R. Accad. Lincei*, 1923, *ii*, **22**, 579 ; Huss and Klemm, *Z. anorg. Chem.*, 1950, **262**, 25 ; Bode, Jenssen and Bandte, *Angew. Chem.*, 1953, **65**, 304), the pentafluorides, $MMnF_5$ (Sharpe and Woolfe, *J. Chem. Soc.*, 1951, 798) and the hexachlorides M_2MnCl_6 (Weinland and Dinkelacker, *Z. anorg. Chem.*, 1908, **60**, 173; Olsson, *Arkiv Kem. Min. Geol.*, 1924, **9**, No. 10, 5). A series of complex iodates $M_2\ Mn(IO_3)_6$ has been described by Berg (*Compt. rend.*, 1899, **128**, 674). Yakimach (*ibid.*, 1930, **190**, 681) obtained a complex cyanide of composition $K_4Mn(CN)_6$ in the form of red crystals, which hydrolysed almost immediately in water and was decomposed by concentrated acids as also on keeping in alcohol. It might as well be represented as a crystal aggregate of $K_2[Mn(CN)_6]$ and 2KCN, since the covalency of manganese is usually limited to six. The oxalato complex of tetrapositive manganese,

$K_2[Mn(C_2O_4)_2(OH)_2]$. $2H_2O$, reported by Cartledge and Ericks (*J. Amer. Chem. Soc.*, 1936, **58**, 2069), decomposes rapidly at room temperature and is stable only in the cold and in the absence of light. In aqueous solution it readily changes into trioxalato manganiate (III). The crystals are reported to be of two colours, green and orange, and are believed to represent the *cis-trans* isomeric modifications. The dark red colour formed, when freshly precipitated manganese dioxide dissolves in alkaline tellurate, is reported to be due to a manganese^{IV} tellurate compound of unknown constitution (Tourky, Issa and Hewaidy, *Anal. Chim. Acta*, 1957, **16**, 151).

These complexes are all of anionic character, and no cationic complexes of tetrapositive manganese have yet been reported. Besides, manganese in its higher oxidation states has not been known to show any perceptible affinity for combination with nitrogen. Recently, however, we have succeeded in isolating a series of cationic tetrapositive manganese complexes with the metal atom linked to the nitrogen atoms of ligands like biguanide and ethylenedibiguanide.

In a previous paper (this *issue*, p. 595) during the preparation of manganese^{III} biguanide base, an orange-red solution was obtained from which the complex tetrapositive manganese base, $[(OH)_2Mn^{IV}(BigH)_2](OH)_2$ separated in the form of bright red crystals. The same compound can be more conveniently obtained by treating a strongly alkaline solution of an excess of biguanide with potassium permanganate either in the presence or absence of ether. Potassium permanganate is reduced *in situ* by ether or/and by a portion of biguanide, first to the green manganate and finally to tetrapositive manganese which is immediately complexed by the excess of biguanide. A third method for its preparation is based on the oxidation of a strongly alkaline mixture of biguanide and manganous sulphate with hydrogen peroxide or sodium persulphate. From the complex base the corresponding nitrate was prepared, and from the latter other salts like the sulphate, chromate, phosphate, oxalate, iodate and fluoberyllate were obtained by metathesis with the appropriate alkali salts. The nitrate in aqueous solution dissociates into three ions, as might be expected, with an equivalent conductivity of about 148 mhos (vide Table II). The variation of λ_v-value with dilution indicates that the complex suffers slight hydrolysis:

$$[(OH)_2Mn^{IV}(BigH)_2]^{2+} + H_2O \rightleftharpoons [(OH)(H_2O)Mn^{IV}(BigH)_2]^{3+} + OH^-.$$

The mobility of the complex ion was found to be 77.1 approx., the conductance of nitrate ion being 71.4.

The complex base of tetrapositive manganese with ethylenedibiguanide, $[(OH)_2Mn^{IV}Et(Big)_2].1.5H_2O$ (where $Et(BigH)_2$ = a molecule of ethylenedibiguanide), was prepared by oxidising a mixture of an alkaline solution of the dibiguanide and manganous sulphate with sodium persulphate. The substance forms sparingly soluble reddish brown crystals which appear violet under the microscope. The same product is formed when an alkaline solution of the dibiguanide is treated with a solution of potassium permanganate. All attempts to prepare the corresponding salts were unsuccessful.

The valency state of manganese in these complexes has been determined by oxidimetric titrations both against sodium thiosulphate (iodometry) and ferrous sulphate solutions. Their magnetic moments, which were expected to substantiate the titrimetric results, however, present some interesting features, as is evident from the following values.

Magnetic moments of Mn^{IV} *biguanide complexes.*

Substance.	Temp.	Magnetic moment. (μ_B).
X $(OH)_2$	30.0°	2.49
X $(NO_3)_2$	29.2°	2.05
X $(SO_4) . 4.5H_2O$	29.8°	2.31
X $(HPO_4) . 1.5H_2O$	29.6°	2.38
X $(C_2O_4) . 0.5H_2O$	29.8°	2.25
X $(CrO_4) . 3H_2O$	29.6°	2.00
X $(IO_3)_2 . 2H_2O$	25.0°	2.20
$[(OH)_2 Mn^{IV} Et (Big)_2] . 1.5H_2O$	29.2°	2.50

X denotes $[(OH)_2 Mn^{IV} (BigH)_2]$.

It should be mentioned that since Mn^{4+}-ion contains three 3*d* electrons (all unpaired) there are two vacant 3*d* orbitals available for bond formation. Magnetic moment would therefore provide no basis for distinguishing between ionic and covalent bonds, since both types of binding would leave three unpaired electrons and, hence, would give the same moment value. The magnetic moments of manganese (IV) compounds, as are available in the literature, viz., K_2MnF_6 ($\mu_B = 3.88$; Wiedemann, *Ann. Physik u. Chem.*, 1887, **32**, 452), K_2MnCl_6 ($\mu_B = 3.89$; Bhatnagar *et al.*, *Proc. Ind. Acad. Sci.*, 1939, **10A**, 150), $K_2Mn(IO_3)_6$ ($\mu_B = 3.82$; Goldenberg, *Trans. Faraday Soc.*, 1940, **36**, 847) are in close agreement with the predicted value of 3.87 Bohr magnetons. A value of $\mu_B = 2.79$ for $K_2[Mn^{IV} (C_2O_4)_2 (OH)_2]$ reported by Grey (*J. Amer. Chem. Soc.*, 1946, **68**, 605) is, however, of doubtful significance ; for the measurement of its magnetic susceptibility was made at 30°, while it is stated in the original paper (Cartledge and Ericks, *loc. cit.*) that the compound decomposes rapidly at room temperature. The observed reduction in the moment value of the biguanide complexes, the purity of which there is no reason to doubt, seems to indicate that the unpaired electrons in the 3*d* orbitals fail to behave normally. The discrepancy observed in the case of MnO_2 ($\mu_B = 2.86$; Grey, *loc. cit.*) has been accounted for by assuming that secondary cation to cation bonds are formed through the overlapping of inter-axial orbitals in the crystal lattice of MnO_2. An interaction of this type would naturally deplete the unpaired electrons of Mn^{IV} ions and, hence, would lower the magnetic moment. The discrepancy observed in the manganese^{IV} biguanide complexes, noted above, must be due to some mechanism similar to that of MnO_2. It is tantamount to saying that metallic bonds are formed, as has been suggested in the case of some compounds of rhenium, a congener of manganese (Schuth and Klemm, *Z. anorg. allgem. Chem.*, 1934, **220**, 193 ; Sen and Rây, this *Journal*, 1953, **30**, 171). Even in the case of oxide, sulphide, selenide and telluride of bipositive manganese, moment values (2.8 – 3.8 μ_B at room temperature) very much lower than the theoretical value of 5.9 Bohr magnetons, have been reported, which suggests the

formation of metallic bonds. This is further supported by the fact that their moment values increase with increasing temperature, as the break-up of metal-metal bonds would require. The formation of similar metallic bonds in the case of manganese (IV) biguanide complexes also is further supported by the observation that the μ_s value of 2.05 of the solid complex nitrate rises to 3.14 in solution, which approaches the theoretical value of 3.87 for quadrivalent manganese. Obviously, the metallic bonds break up in solution. A measurement of the temperature variation of the susceptibility of the solid complex nitrate has furnished additional evidence for this assumption. A linear decrease in the effective Bohr magneton value from the room temperature (300°K) down to 140°K, contrary to Curie-Weiss law, has been observed (vide Fig. 2). From a consideration of their physical and chemical behaviour they may therefore be regarded as penetration or inner-level octahedral complexes due to d^2sp^3 hybrid bonds, with development of metal-metal linkages in the solid crystalline state.

EXPERIMENTAL

Dihydroxo Manganese^{IV} bis-*Biguanide Dihydrate*

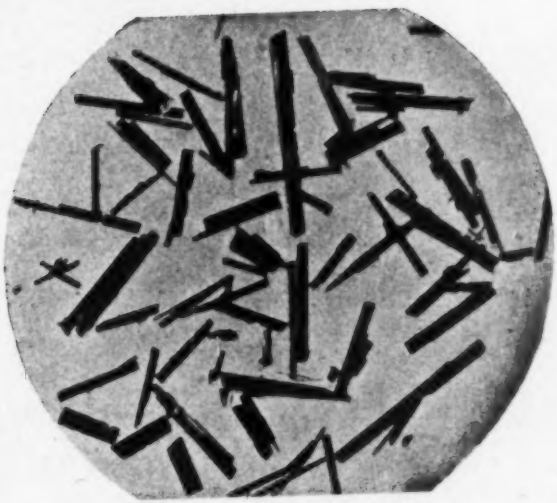
A. Reaction with Potassium Permanganate.—A solution of $KMnO_4$ (0.8 g. in 25 c.c. of water) was added dropwise with constant stirring to that of biguanide acid sulphate (5.5 g. in 75 c.c. of 4% NaOH solution). The colour of the permanganate first changes to green (manganate) and finally to dark orange-red. The reduction of permanganate is slow to begin with and gradually becomes rapid The resulting dark orange-red solution, along with some crystals that separated, was cooled in an ice-bath for about an hour. The mixture was then filtered in a sintered glass crucible and the crystals were washed with ice-cold water. These were sucked dry on the pump and kept in a vacuum desiccator over $CaCl_2$ and KOH. The next day the crystals were taken out and kept in air, free from carbon dioxide, to acquire a constant weight ; yield 1.2 g., representing about 75% of the manganese in the permanganate used

The first crop of the compound which separated immediately in quantities was made up of fine crystals. The mother-liquor on being cooled in an ice-bath deposited a second crop of lustrous needles. The best-sized crystals were obtained by allowing the solution to evaporate slowly in air at room temperature (vide microphotograph, Fig. 1).

The compound has also been prepared from manganous sulphate and biguanide sulphate by oxidation with hydrogen peroxide or sodium persulphate in alkaline medium.

B. Oxidation with Hydrogen Peroxide.—Biguanide acid sulphate (7 g.), dissolved in 8% NaOH solution (50 c.c.) was filtered by suction and the filtrate collected in a flask. A solution of manganous sulphate $MnSO_4.4H_2O$ (1 g. in 10 c.c. of water) was added to it, when manganous hydroxide was precipitated. The mixture was cooled in an ice-bath to 10°–15° ; 4 c.c. of '20 vol'. hydrogen peroxide was slowly added in portions, while briskly shaking the flask and its contents. The flask was then taken out of the ice-bath and shaken frequently until a dark red solution was obtained. This was filtered by suction immediately. The dark red crystals of the substance separated in quantities on cooling the filtrate in ice for about an hour. These were filtered, washed and dried as described before ; yield 1.3 g.

FIG. 1



Microphotograph of the crystals of Dihydroxo Manganese (IV) *bis*-biguanide dihydrate.

C. Oxidation with Sodium Persulphate.—To a cooled solution of biguanide acid sulphate (7 g.) in 8% NaOH solution (50 c.c.) was added dropwise with stirring a solution of manganous sulphate (1 g.) and sodium persulphate (3 g.) in 20 c.c. of water. At the end of the addition the bright red solution was filtered and the filtrate was cooled in ice for about an hour ; yield 1.3 g.

{Found : Mn, 16.82, 16.84 ; O (active), 4.90 ; N, 43.06 ; H_2O (by loss at 90°), 11.10. $[(OH)_2\ Mn^{IV}\ (BigH)_2](OH)_2$ requires Mn, 16.90 ; O (active), 4.92 ; N, 43.07 ; H_2O, 11.08%}. {Found (for the vacuum-dried sample) : O (active), 5.47. Found (for the sample dried at 90°) : O (active), 5.53. Calc. for the dehydrated sample $[(OH)_2\ Mn^{IV}(Big)_2]$: O (active), 5.54%}. Oxidimetric titration indicated that the substance suffered partial decomposition at 100°.

The product forms dark red crystals, sparingly soluble in water, giving an orange-red solution. The aqueous solution is alkaline to litmus ($p_H \sim 8$) and is quite stable at room temperature. The solution remains clear for several hours after which it turns turbid due to the separation of manganese dioxide. On keeping in vacuum or by heating at 90°, the compound loses two molecules of water. At higher temperature slow decomposition sets in. The colour of the dehydrated sample is dark chocolate-red. On exposure to air it regains its original weight and colour.

Magnetic Susceptibility : $\chi_g = 7.435 \times 10^{-6}$; $\chi_M = 2416 \times 10^{-6}$; diamagnetic correction $= +\ 123 \times 10^{-6}$; χ_M (cor.) $= 2539 \times 10^{-6}$; μ_B (effective) = 2.49 (30°).

Dihydroxo Manganese^{IV} bis-*Biguanidinium Nitrate*

The complex base (1 g.) was suspended in cold water (100 c.c.) in which it partially dissolved. Dilute acetic acid was added dropwise to it with stirring until a dark reddish brown solution (p_H 4–6) was obtained. It was filtered from any residual impurities. To the clear filtrate a solution of potassium nitrate (5 g. in 20 c.c. of water) was added when a flocculent precipitate was obtained. This was allowed to stand in an ice-bath. The precipitate gradually became crystalline and settled down. The crystals were filtered, washed and dried as usual. {Found : Mn 13.47, 13.33 ; O (active), 3.89, 3.90 ; N, 42.2 ; NO_3, 31.06. $[(OH)_2Mn^{IV}(BigH)_2](NO_3)_2$ requires Mn, 13.23 ; O (active), 3.85 ; N, 40.49 ; NO_3, 29.88%}.

The product forms dark chocolate (almost black) shining crystals. It is readily soluble in water, giving a reddish brown faintly acid solution. Measurement of the conductivity values indicates that the complex is fairly stable in solution for 2–3 hours, but slightly hydrolyses in dilute solutions.

Magnetic Susceptibility : (A) In the solid state.—$\chi_g = 3.832 \times 10^{-6}$; $\chi_M = 1591 \times 10^{-6}$; diamagnetic correction $= +\ 134.8 \times 10^{-6}$; χ_M (cor.) $= 1725.8 \times 10^{-6}$; μ_B (effective) = 2.05 (29.2°).

(*B*). *In solution.*—$\chi_{g\ (solution)} = -0.7092 \times 10^{-6}$ ($C_{solution}$ = 0.377 g./50 g. of water) ; $\chi_{g\ (salt)} = 9.378 \times 10^{-6}$; $\chi_M = 3892 \times 10^{-6}$; χ_M (cor.) $= 4027 \times 10^{-6}$; μ_B (effective) = 3.14 (31°).

Study of the Variation of Magnetic Susceptibility with Temperature.—A modified Curie balance (Dutta Ray, *Indian J. Phys.*, 1956, **30**, 167) and a liquid air cryostat were used to determine accurately the value of the susceptibility of the sample at room temperature (300°K) by comparison with that of chrome potassium alum crystal, standardised against a standard $NiCl_2$ solution. The magnetic force on the sample, mounted at the end of the horizontal balance-arm and placed in a vertical magnetic field with a horizontal gradient, was balanced accurately by twisting the vertical quartz fibre from which the balance beam is suspended. The forces at the other constant temperatures down to 140°K, were then measured, retaining all other conditions, e.g., suspension, magnetic field etc., the same as at the room temperature. The results of measurement are shown in Fig. 2 and Table I.

FIG. 2

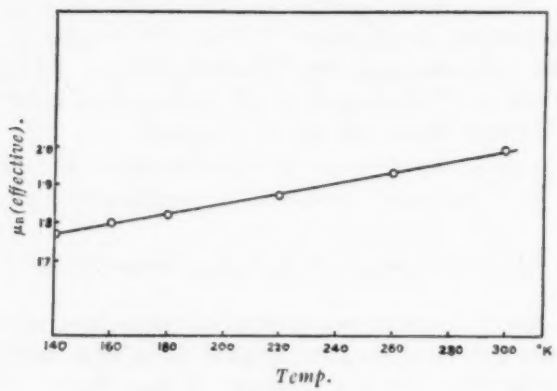


TABLE I

Temp.	$\chi_M \times 10^6$.	χ_M (cor.) $\times 10^6$.	μ_B (effective).
300° K	1517.2	1652	1.995
260°	1640 2	1775	1.931
220°	1843.2	1978	1.874
180°	2151.2	2286	1 818
160°	2377.2	2512	1.796
140°	2657.2	2792	1.768

Conductivity Measurements.—Solutions of the complex nitrate in different dilutions were made with conductivity water. The conductance of these solutions was measured in a conductivity cell, whose cell constant was determined previously. The equivalent conductivity at infinite dilution was calculated from Walden's formula,

$$\lambda_\infty = \lambda_v (1 + 0.692 \times n_1 n_2 \times v^{-\frac{1}{2}}),$$

where n_1 and n_2 are the valencies of the ions. The results are shown in Table II.

TABLE II

Cell constant = 1.503. Temp. = 29°.

Dilution in litres (v).	Conductance (μ).	Equivalent conductivity (λ_v).	Equivalent conductivity at infinite dilution (λ_∞).
64	0.1 × 10^{-4} mho	96.2	112.8
128	5.4 × 10^{-5}	102.0	114.5
256	3.2 × 10^{-5}	123.1	133.8
512	1.73 × 10^{-5}	133.1	141.2
1024	0.93 × 10^{-5}	142.3	148.5

The variation of λ_∞-value with dilution signifies progressive hydrolysis.

Dihydroxo Manganese^{IV} bis-*Biguanidinium Sulphate*

The complex base (1 g.), mixed with cold water (20 c.c.), was treated with dilute nitric acid (3 *N*) dropwise until a clear solution was obtained (p_H 4–6). The solution was filtered. To the filtrate 5% ammonium sulphate solution was added dropwise with stirring until a precipitate just appeared. The mixture was cooled in ice for half an hour. The shining silky crystals of the complex sulphate separating were filtered, washed and dried as usual. The same product was obtained by treating an aqueous solution of the pure complex nitrate with ammonium sulphate ; yield 0.9 g. {Found : Mn, 11.69, 11.75 ; O (active), 3.43 ; N, 30.14 ; SO_4, 20.35 ; H_2O (by loss at 90°), 17.18. $[(OH)_2\ Mn^{IV}\ (BigH)_2]SO_4\ 4.5H_2O$ requires Mn, 11.75 ; O (active), 3.42 ; N, 29.91 ; SO_4, 20.51 ; H_2O, 17.31%}. [Found for the sample dehydrated at 90° : O (active), 4.09. Calc. : O (active), 4.13%].

The product ordinarily forms snuff-coloured crystalline powder, sparingly soluble in water, giving a light-yellow, faintly acid solution. The compound is fairly stable at room temperature in the dry state.

Magnetic Susceptibility : $\chi_g = 4.268 \times 10^{-6}$; $\chi_M = 1997 \times 10^{-6}$; diamagnetic correction = + 195.5 × 10^{-6} ; χ_M (cor.) = 2192.5 × 10^{-6} ; μ_B (effective) = 2.314 (29.8°).

Dihydroxo Manganese^{IV} bis-*Biguanidinium Hydrogen Phosphate*

To the filtered solution of the complex nitrate (1 g.) in cold water (20 c.c.) a solution of disodium hydrogen phosphate (1 g. in 10 c.c. of water) was added dropwise with stirring until a slight turbidity appeared. The mixture was cooled in ice for about half an hour. The crystals of the complex phosphate separating were filtered, washed and dried as usual ; yield 0.9 g.

For the estimation of total manganese and phosphate, the complex was decomposed by digesting with dilute alkali on the water-bath and filtered. The residual manganese dioxide was dissolved in HCl (dil.) and manganese was precipitated as $MnNH_4PO_4$. From the combined filtrate and washings phosphoric acid was precipitated as $MgNH_4PO_4$. {Found : Mn, 13.22 ; O (active), 3.88, 3.85 ; PO_4, 22.44. $[(OH)_2Mn^{IV}\text{-}(BigH)_2](HPO_4)\cdot 1.5H_2O$ requires Mn, 13.26 ; O (active), 3.86 ; PO_4, 22.92%}. It resembles the sulphate in properties.

Magnetic Susceptibility : $\chi_g = 5.217 \times 10^{-6}$; $\chi_M = 2160 \times 10^{-6}$; diamagnetic correction = + 159 × 10^{-6} ; χ_M (cor.) = 2319 × 10^{-6} ; μ_B (effective) = 2.38 (29.6°).

Dihydroxo Manganese^{IV} bis-*Biguanidinium Oxalate*

This was obtained as a chocolate-brown crystalline precipitate from a solution of the complex nitrate by adding a solution of sodium oxalate.

For analysis, the sample was decomposed by boiling with dilute alkali. Precipitated manganese dioxide was filtered off and in the filtrate oxalic acid was estimated by titration with permanganate as usual. Manganese was estimated as $MnSO_4$. {Found: Mn, 14.07; O (active), 4.12; $(COO)_2$, 22.2. $[(OH)_2\ Mn^{IV}\ (BigH)_2](COO)_2.0.5\ H_2O$ requires Mn, 14.16; O (active), 4.12; $(COO)_2$, 22.69%}.

Magnetic Susceptibility: $\chi_g = 4.989 \times 10^{-6}$; $\chi_M = 1936 \times 10^{-6}$; diamagnetic correction = + 131 × 10^{-6}; χ_M (cor.) = 2067 × 10^{-6}; μ_B (effective) = 2.247 (29.8°).

Dihydroxo Manganese^{IV} bis-*Biguanidinium Chromate*

This was prepared by double decomposition of the complex nitrate with potassium chromate.

For the estimation of total manganese and chromium, the complex was decomposed with dilute alkali. The precipitated manganese dioxide was filtered. In the filtrate chromate was determined in the usual way by titration against ferrous ammonium sulphate. The residue was dissolved in HCl and manganese was precipitated as $MnNH_4PO_4$. {Found: Mn, 11.80; CrO_4, 25.27; active oxygen (total), 8.71; N, 30.01%. $[(OH)_2\ Mn^{IV}\ (BigH)_2]CrO_4.3H_2O$ requires Mn, 11.94; CrO_4, 25.16; active oxygen (total), 8.68; N, 30.37%}.

The product forms snuff-coloured crystals sparingly soluble in water, giving a light yellow solution.

Magnetic Susceptibility: $\chi_g = 3.561 \times 10^{-6}$; $\chi_M = 1642 \times 10^{-6}$; diamagnetic correction = + 116 × 10^{-6}; χ_M (cor.) = 1758 × 10^{-6}; μ_B (effective) = 2.07 (29.6°).

Dihydroxo Manganese^{IV} bis-*Biguanidinium Iodate*

The complex base (1 g.) was mixed with cold water (50 c.c.) and the mixture was treated dropwise with dilute acetic acid until a dark reddish brown solution (p_H 4–6) was obtained. It was filtered to remove any residual impurity. To the clear filtrate an almost saturated solution of potassium iodate (2 g. in 25 c.c. of water) was added with stirring, when the solution became slightly hazy. The mixture was cooled in an ice-bath for about an hour. The small chocolate-coloured glistening crystals that separated were filtered, washed with ice-cold water and dried as usual

Iodate was estimated by reducing the sample with sulphur dioxide in sulphuric acid medium to iodide which was then precipitated as AgI. {Found: Mn, 8.10; active oxygen (total), 16.39; IO_3, 51.53; H_2O (by loss in vacuum), 5.77. $[(OH)_2\ Mn^{IV}(BigH)_2]\ (IO_3)_2.2H_2O$ requires Mn, 8.12; active oxygen (total), 16.54; IO_3, 51.70; H_2O, 5.32%}.

Magnetic Susceptibility: $\chi_g = 2.665 \times 10^{-6}$; $\chi_M = 1804 \times 10^{-6}$; diamagnetic correction = + 199.8 × 10^{-6}; χ_M (cor.) = 2003.8 × 10^{-6}; μ_B (effective) = 2.195 (25°).

Dihydroxo Manganese^{IV} bis-*Biguanid nium Fluoberyllate*

The complex fluoberyllate was prepared by treating a solution of the complex nitrate with a concentrated solution of ammonium fluoberyllate and cooling the mixture in an ice-bath. The substance on qualitative analysis was found to contain Be and F, giving characteristic reactions of BeF_4^{2-} ion. { Found : Mn, 12.42 ; O (active), 3.60. $[(OH)_2\ Mn^{IV}\ (BigH)_2]\ BeF_4.3.5\ H_2O$ requires Mn, 12.51 ; O (active), 3.64% }.

The product forms fairly soluble cinnamon-coloured crystals.

Dihydroxo Manganese^{IV} Ethylenedibiguanide Hydrate

Ethylenedibiguanidinium sulphate (4 g.) (Chakravarty and Rây, this *Journal*, 1944, 21, 441) was dissolved in 15% NaOH solution (60 c.c.) and filtered. To the filtrate a solution of manganous sulphate (1 g.) and sodium persulphate (3 g.) in 20 c.c of water was added with stirring. A dark reddish brown solution was obtained. This was immediately filtered by suction to remove any precipitated manganese dioxide. The filtrate was then cooled in ice for about half an hour. Reddish brown crystals separating were filtered, washed with ice-cold water and dried in vacuum over $CaCl_2$ and KOH. { Found : Mn, 16.04 ; O (active), 4.63, 4.67 ; N, 40.56, 40.79. $[(OH)_2\ Mn^{IV}$-$Et(Big)_2]\ 1.5\ H_2O$ requires Mn, 16.05 ; O (active), 4.67 ; N, 40.94% }.

The product forms reddish brown crystals, sparingly soluble in water, giving a reddish brown solution which reacts alkaline to litmus ($p_H \sim 8$). Addition of alkali salt solution to a solution of the complex base, acidified with dilute acetic acid, produces an opalescence. The compound is quite stable both in the solid state and in solution at room temperature.

Magnetic Susceptibility : $\chi_g = 7.087 \times 10^{-6}$; $\chi_M = 2423.8 \times 10^{-6}$; diamagnetic correction $= + 140.2 \times 10^{-6}$; χ_M (cor.) $= 2564 \times 10^{-6}$; μ_M (effective) $= 2.50$ (29 2°).

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BEHAVIOUR OF NITROPHENOLS WITH *p*-TOLUENESULPHONYL CHLORIDE. PART VII. ABNORMAL BEHAVIOUR OF 3:6-DICHLORO- AND 3:6-DIBROMO-2:4-DINITROPHENOLS

By Shiam Sunder Joshi and Tara Chand Mathur

Ordinarily in dinitrophenols the hydroxyl group is replaced by a chlorine atom when heated with *p*-toluenesulphonyl chloride and diethylaniline. 3:6-Dichloro-2:4-dinitrophenol and 3:6-dibromo-2:4-dinitrophenol have failed to give the chloro compounds and also the esters.

Most nitrophenols that have at least two nitro groups in *ortho*:*para* positions with respect to the hydroxyl group, when heated with *p*-toluenesulphonyl chloride in presence of diethylaniline, form the corresponding chloropolynitrobenzenes together with varying amounts of *p*-toluenesulphonic esters of the phenols (Ullmann *et al.*, *Ber.*, 1908, **41**, 1870; 1911, **44**, 3731). Of these two products, the former is more reactive than the other. Both the ester and the chloropolynitrobenzene, so obtained, when treated with ammonia, dimethylamine, piperidine, etc., yield identical amino, dimethylamino, piperidino, etc. derivatives.

A few dinitrophenols and their esters, however, were found to behave differently. Not only they failed to yield under similar conditions the corresponding chlorodinitrobenzenes, but even the esters that they formed were unreactive. Thus, 4-chloro-2:6-dinitro-3-methylphenol (*J. Chem. Soc.*, 1924, 2481), 3:6-dimethyl-2:4-dinitrophenol (this *Journal*, 1932, **9**, 59), 4-bromo-2:6-dinitro-3-methylphenol (*ibid.*, 1949, **26**, 539), 4:6-dinitrothymol (*ibid.*, 1932, **9**, 55), 2:4-dinitrocarvacrol (*loc. cit.*) failed to afford the corresponding chloro compounds, but yielded the esters. The esters also were found to be quite stable and did not behave like the esters of other polynitrophenols.

In the present investigation two dinitrophenols, 3:6-dichloro- and 3:6-dibromo-2:4-dinitrophenols, have been examined. With *p*-toluenesulphonyl chloride in presence of diethylaniline, they neither furnish the corresponding chloro compounds nor the esters. In each case, the original compounds were recovered. Their esters, however, have been obtained by the interaction of their sodium salts with *p*-toluenesulphonyl chloride. These on being allowed to react with ammonia, dimethylamine, piperidine, *p*-toluidine, etc. undergo hydrolysis and at the same time the chlorine in the *meta* position is replaced. In the case of their methyl ethers, the methoxy group remains intact and the halogen atom in the *meta* position is substituted. This behaviour does not appear to be quite normal and due to steric factor only, as in compounds like 2-chloro (or bromo)- and 3-chloro-4:6-dinitrophenols, replacement of the hydroxyl group by a chlorine atom takes place under similar experimental conditions.

EXPERIMENTAL

3 : 6-*Dichloro-4-nitrophenol and* 3 : 6-*Dichloro-2* : 4-*dinitrophenol.*—3:6 Dichloroaniline (20 g.), dissolved in H_2SO_4 (*d* 1.84, 75 c.c.), was diazotised with sodium nitrite (10 g.) in H_2SO_4 (*d* 1.84, 75 c.c.). The product on keeping and subsequently heating after dilution with 75 c.c. of water gave a solid which on recrystallisation from acetic acid furnished 3 : 6-dichlorophenol (12-15 g.), m.p. 58°. This (11 g.) on nitration in acetic acid solution with smaller amounts of nitrtc acid afforded 3 : 6-dichloro-4-nitrophenol (3.5 g.), m.p. 115° (cf. Kehrmann, *Ber.*, 1888, **21**, 3319). Acetyl derivative, m.p. 89° ; benzoyl derivative, m.p. 86° ; monobromo derivative, m.p. 135°. With excess of nitric acid it furnished 3 : 6-dichloro-2 : 4-dinitrophenol which was recrystallised from acetic acid, m.p. 146° (cf. Fries, *Annalen*, 1927, **454**, 247) ; acetyl derivative, m.p. 94° and benzoyl derivative, m.p. 118°.

3 : 6-*Dichloro-2* : 4-*dinitrophenyl* p-*Toluenesulphonate.*—Sodium salt of 3 : 6-dichloro-2 : 4-dinitrophenol and *p*-toluenesulphonyl chloride in molecular proportions were heated at 120-40° for a few minutes. The product from alcohol gave colorless crystals, m.p. 121°. (Found : Cl, 17.2 ; S, 7.96. $C_{13}H_8O_7N_2Cl_2S$ requires Cl, 17.4 ; S, 7.86%).

3 : 6-*Dichloro-2* : 4-*dinitrophenyl Methyl Ether.*—3 : 6-Dichloroanisole (m.p. 24°), obtained by methylation of 3 : 6-dichlorophenol, when treated in acetic acid with smaller amounts of HNO_3 (*d* 1.42, cold), yielded 3 : 6-dichloro-4-nitroanisole, m.p. 101° (Kohm and Fink, *Monatsh.*, 1931, **58**, 73). This, when further nitrated at room temperature in H_2SO_4 (*d* 1.84) with a mixture of equal quantities of fuming nitric acid (*d* 1.52) and concentrated nitric acid (*d* 1.42), gave 3:6-dichloro-2 : 4-dinitrophenyl methyl ether, which was recrystallised from alcohol, m. p. 61° (*loc.cit.*). 3 : 6-Dichloro-2 : 4-dinitrophenol with dimethyl sulphate did not form any methyl ether under usual conditions.

Derivatives from 3 : 6-*Dichloro-2* : 4-*dinitrophenol, its* p-*Toluenesulphonate and its Methyl Ether*: 1-*Hydroxy-2* : 4-*dinitro-6-chlorodiphenylamine.*—3 : 6-Dichloro-2 : 4-dinitrophenol (2 g.), aniline (5 c.c.), alcohol (3-4 c.c.) and a little fused sodium acetate were refluxed together for 1½ hours in a boiling water-bath. On acidifying with HCl (dil.) a red derivative separated, which was recrystallised from alcohol, m.p. 140°. (Found : N, 14.08 ; Cl, 10.95. $C_{12}H_8O_5N_3Cl$ requires N, 13.6 ; Cl, 11.4%). Acetyl derivative, m.p. 115°. The identical compound was obtained from 3:6-dichloro-2 : 4-dinitrophenyl *p*-toluenesulphonate under similar conditions. Derivatives from other amino compounds are shown in Table I.

TABLE 1

Compounds.	M. P. of the derivatives from Aniline.	Dimethylamine.	Piperidine.	*p*-Toluidine.
3 : 6-Dichloro-2 : 4-dinitrophenol	140°	118°	138°	148°
3 : 6-Dichloro-2 : 4-dinitrophenyl *p*-toluenesulphonate	140°	117°	138°	148°
3 : 6-Dichloro-2 : 4-dinitrophenyl methyl ether	138°	110°	136°	144°

1-Methoxy-6-chloro-2 : 4-dinitrodiphenylamine.—3 : 6-Dichloro-2 : 4-dinitrophenyl methyl ether (2 g.), aniline (5 c.c.), alcohol (3-4 c.c.) and a little fused sodium acetate were refluxed together for about 2 hours in a boiling water-bath. On treatment with HCl (dil., 1 : 1), a red derivative separated, which was recrystallised from alcohol, m.p. 138°. (Found : N, 13.07 ; Cl, 10.62. $C_{13}H_{10}O_5N_3Cl$ requires N, 12.98 ; Cl, 10.95%). Derivatives from other amino compounds are recorded in Table I.

All these amino derivatives were recrystallised from alcohol. The compounds obtained from the phenol and its *p*-toluenesulphonate with different bases are soluble in dilute sodium carbonate solution, while those from the methyl ether fail to dissolve. The derivatives from the phenol and its *p*-toluenesulphonate with different bases are identical in each case and are different from those similarly obtained from the methyl ether. This was also confirmed by the mixed melting point determinations.

3 : 6 Dibromo-2-nitrophenol and 3 : 6-Dibromo-2 : 4-dinitrophenol.—3 : 6-Dibromophenol, prepared from 3 : 6-dibromoaniline in the same manner as 3:6-dichlorophenol from its corresponding aniline, on nitration in cold in acetic acid solution with a small quantity of HNO_3 (*d* 1.42), gave a product, which after neutralisation with sodium carbonate and subsequent decomposition by dilute hydrochloric acid, afforded a solid, which on crystallisation from dilute acetic acid (1 : 3) furnished 3 : 6-dibromo-2-nitrophenol. It was recrystallised from 75% alcohol, m.p. 77° (Jackson and Calhane, *J. Amer. Chem. Soc.*, 1906, **28**, 472).

When 3 : 6-dibromophenol was nitrated in cold in acetic acid with a little excess of nitric acid (*d* 1.42), 3 : 6-dibromo-2 : 4-dinitrophenol was obtained. It was crystallised from alcohol, m.p. 123°.

3:6-Dibromo-2 : 4-dinitrophenyl p-toluenesulphonate was prepared from 3 : 6-dibromo 2 : 4-dinitrophenol in the same way as 3 : 6-dichloro-2 : 4-dinitrophenyl *p*-toluenesulphonate (*vide supra*) and recrystallised from alcohol, m.p. 138°.

The derivatives obtained from both 3 : 6 dibromo-2 : 4-dinitrophenol and its *p*-toluenesulphonate with different bases, such as aniline, *o*- and *p*-toluidines and piperidine, in alcoholic solutions in presence of anhydrous sodium acetate, were found to be identical in each case, as shown by their melting points and their mixed melting points.

TABLE II

Compounds.	M.P. of the derivatives from Aniline.	*o*-Toluidine.	*p*-Toluidine.	Piperidine.
3 : 6-Dibromo-2 : 4-dinitrophenol	135°	141°	145°	132°
3 : 6-Dibromo-2 : 4-dinitrophenyl *p*-toluenesulphonate	135°	142°	145°	132°

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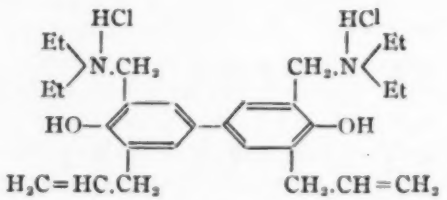
POSSIBILE ANTIAMOEBIC AGENTS. PART VII. ANALOGUES OF CAMOFORM

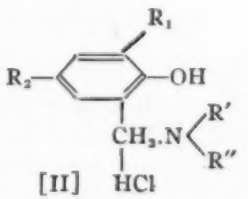
By A. B. Sen and S. L. Arora

Several Mannich base hydrochlorides have been synthesised from substituted allylphenols with a view to testing them for their antiamoebic activity.

Recently Park Davis & Co. has introduced camoform as an effective amoebacide. It was first synthesised as a possible antimalarial by Burckhalter *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1894). Clinical trials by Hoekenga *et al.* (*Am. J. Trop. Med. & Hyg.*, 1954, **3**, 849) revealed it to be a non-toxic amoebacide, the cure rate being as high as 85%. Structurally, camoform is the dihydrochloride (I) of the Mannich base, derived from 4 : 4′-dihydroxy-3 : 3′-diallyldiphenyl. In the present investigation a number of Mannich base hydrochlorides (II), analogous to camoform, have been synthesised from unsaturated phenols, containing an allyl or propenyl grouping and another substituent (chloro, methyl, *tert.*-butyl or methoxy) with a view to studying the effect of simplifying the camoform molecule in relation to its antiamoebic activity.



[I]



[II]

[R_1 & R_2 = substituents in the nucleus ; R′ & R″ = substituents in the basic side chain].

The allylphenols were prepared by the Claisen rearrangement of the corresponding allyl phenyl ethers.

Mannich base hydrochlorides have been prepared from eugenol (*o*-methoxy-*p*-allylphenol), *o*-allyl-*p*-methyl-, *o*-allyl-*p*-chloro- and *o*-allyl-*p*-*tert.*-butyl-phenols, using formaldehyde and different amines, viz., benzylamine, morpholine, piperidine and piperazine, following the method of Bruson *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 270).

TABLE I

Sl. No.	R_1 & R_2.	R' & R''.	Mannich base hydrochloride M.P.	% Yield	Formula.	% Nitrogen Found.	% Nitrogen Calc.	Picrates M.P.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	2-Methoxy-4-allyl-	Benzyl-	167-68°	74	$C_{18}H_{22}O_2NCl$	4.20	4.38	...	...	...	...
2.	,,	Morpholinyl-	183°	95	$C_{15}H_{22}O_3NCl$	4.72	4.67	134°	$C_{21}H_{24}O_{16}N_4$	11.20	11.38
3.	,,	Piperidyl-	157°	82	$C_{16}H_{24}O_2NCl$	4.60	4.71	148°	$C_{22}H_{26}O_9N_4$	11.30	11.43
4a*	,,	Piperazine	145°	64	$C_{26}H_{34}O_4N_2$	6.26	6.39	...	...	...	...
4b	,,	,,	220°	...	$C_{26}H_{36}O_4N_2Cl_2$	5.58	5.48	...	...	...	...
5.	2-Allyl-4-methyl-	Benzyl-	132°	91	$C_{18}H_{22}ONCl$	4.50	4.61	...	...	...	...
6.	,,	Morpholinyl-	172°	91	$C_{15}H_{21}O_2NCl$	5.10	4.94	162°	$C_{21}H_{24}O_9N_4$	11.60	11.76
7.	,,	Piperidyl-	178°	63	$C_{16}H_{24}ONCl$	4.85	4.97	...	...	...	...
8.	2-Allyl-4-chloro-	Benzyl-	144°	77	$C_{17}H_{19}ONCl_2$	4.25	4.32	...	...	...	...
9.	,,	Morpholinyl-	180°	96	$C_{14}H_{19}O_2NCl_2$	4.51	4.60	187°	$C_{20}H_{21}O_9N_4Cl$	1 .15	11.28
10.	,,	Piperidyl-	175°	90	$C_{15}H_{21}ONCl_2$	4.52	4.63	...			
11a*	,,	Piperazine	179°	60	$C_{24}H_{28}O_2N_2Cl_2$	6.15	6.26	...			
11b	,,	,,	208°	...	$C_{24}H_{30}O_2N_2Cl_4$	5.40	5.39	226°	$C_{36}H_{34}O_{16}N_8Cl_2$	12.20	12.37
12.	2-Allyl-4-*tert*-butyl-	Morpholinyl-	171°	98	$C_{18}H_{28}O_2NCl$	4.42	4.30	204°	$C_{24}H_{30}O_9N_4$	10.65	10.81
13.	,,	Piperidyl-	202°	92	$C_{19}H_{30}ONCl$	4.22	4.33	...	...	...	...
14a*	,,	Piperazine-	150°	51	$C_{32}H_{46}O_2N_2$	5.80	5.71	...	...	...	...
14b	,,	,,	222°	...	$C_{32}H_{48}O_2N_2Cl_2$	4.90	4.97	...	...	...	...

*a-as free Mannich base

b-The hydrochloride of the Mannich base.

EXPERIMENTAL

Mannich Base Hydrochlorides.—A mixture of the substituted phenol (0.01*M*) and the amine (0.013 *M*) was taken in a round-bottomed flask fitted with a reflux condenser, cooled externally by ice. To this was added calculated amount of a 30% aqueous solution of formaldehyde dropwise under stirring in about 20 minutes, when a thick emulsion was obtained. The flask was removed from the cooling bath and the reaction mixture kept at room temperature for half an hour, after which it was refluxed on the water-bath for another 2 hours, when the Mannich base separated out as an oily layer. To this was added the requisite quantity of sodium chloride (A.R.) and the mixture was refluxed again for about 20 minutes. After cooling, it was extracted with ether and the ether extract was separated and dried over anhydrous magnesium sulphate. Dry HCl gas was passed in the cold ether extract, when the Mannich base hydrochloride separated out as a crystalline mass. It was filtered at the pump, washed with dry ether, then with absolute ethyl alcohol, and finally dried. In majority of the cases the Mannich base hydrochlorides, thus obtained, were pure enough and needed no further crystallisation. However, in certain cases, where the melting point was not sharp, recrystallisation was effected with absolute ethyl alcohol or benzene.

It was observed that the Mannich bases, prepared from piperazine (No. 4a, 11a and 14a in Table I), separated as a crystalline solid instead of an oily layer, after 15 minutes of reflux on the water-bath. These were redissolved in absolute ethyl alcohol and refluxed for another 2 hours after which the hydrochlorides were isolated in the usual way by dissolving them either in ether or benzene and passing dry HCl gas. The Mannich base hydrochlorides were characterised through their picrates.

Picrates.—The Mannich base hydrochloride (II, 0.5 g.) (No. 2,3,6 and 9 in Table I) was dissolved in 5 c.c. of hot water. To this was added a slight excess (about 25%) of a saturated aqueous solution of picric acid, when a thick yellow heavy precipitate was obtained. This was boiled gently for sometime and then cooled when the crystalline picrate separated out, which was filtered at the pump, washed with a little alcohol and recrystallised from boiling water.

In certain cases, where the Mannich base hydrochlorides (No. 11 & 12 in Table I) were not soluble in water, these were dissolved in 5 c.c. of rectified spirit and to these 5 c.c. of a cold alcoholic saturated solution of picric acid was added and then warmed on the water-bath for about 5 minutes. On cooling, the picrate separated out which was filtered and recrystallised from alcohol.

The compounds (3,6,9 & 13 in Table I) (0.5 g. each) were dissolved in 5 c.c. of water separately and the aqueous solutions allowed to stand at room temperature for 36 hours. The solutions remained transparent throughout. On removing water from each solution, the original compound was recovered in all the cases. The melting points, yields and analyses of the Mannich base hydrochlorides and their picrates are recorded in Table I.

One of the authors (S.L.A.) expresses his grateful thanks to the U.P. Scientific Research Committee for the award of a research assistantship.

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SHORT NOTES

POTENTIOMETRIC STUDIES ON MERCURY MOLYBDATE

By C. M. Gupta and Ram Sahai Saxena

A survey of literature reveals that there are meagre references on the study of mercury molybdate. Molybdate ion exists in different states of aggregation depending on the p_H of the solution (Jander *et al.*, *Ber.*, 1930, **194**, 383). It is of interest therefore to study the conditions favourable for the precipitation of mercury molybdate by applying electrometric methods.

'AnalaR' (B.D.H.) chemicals were used. Na_2MoO_4 solution was estimated as $MoS_3,2H_2O$ (*Anal. Chim. Acta*, 1953, **9**, 263) and $Hg(NO_3)_2$ was prepared in the minimum amount of HNO_3 (dil.) and was estimated as $[Hg(CNS)_2]$ by titrating against standardised KCNS (Vogel, "A Text Book of Quantitative Analysis", p. 265).

For measurement of E.M.F., Cambridge p_H-meter was used. A bight platinum wire was used as an indicator electrode in conjunction with a saturated calomel electrode. Titrations were done in aqueous and aqueous-alcoholic solutions. Titrations in presence of alcohol were carried out up to a total concentration of 20% by volume. Curves were plotted between the volume of the titrant and the E.M.F. observed. From the sharp jump in the potential, indicated by the titration curve, the end-point could be found out. Mercury nitrate and sodium molybdate were alternately used as the titre, and the titrant was added through a micro-burette. p_H of the solutions was measured using glass electrode of the range 1-13 p_H.

The p_H of Na_2MoO_4 was 7.2 and that of $Hg(NO_3)_2$, 1.3. Dilute solutions used in these experiments were of p_H 2. The molybdate ion is said to exist in the following state of aggregation at different p_H of the solution :

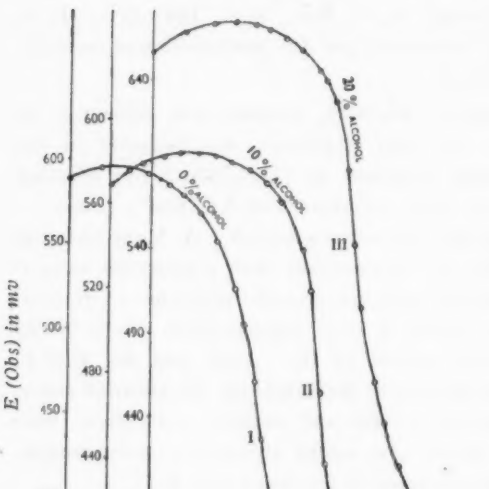
$$MoO_4^{2-} \rightleftharpoons Mo_2O_{11}^{4-} \rightleftharpoons Mo_6O_{21}^{6-}$$

p_H 14 to 6.5 6.5 to 4.5 4.5 to 1.5

All the above ionic species are p_H-reversible. The change from one to another is never sudden. They are supposed to exist in equilibrium. According to Raman Rao (*J. Sci. Ind. Res.*, 1954, **13B**, 739) Ca, Ba, Sr and Cd molybdates are precipitated at p_H 4.18 and below this p_H, no precipitation takes place. But in this case at p_H 2, normal mercury molybdate was precipitated, having the composition $HgO.MoO_3$. The compound on analysis for the molybdate and Mo content gave also the same composition as obtained by potentiometric method. When Na_2MoO_4 is added to $Hg(NO_3)_2$ and the reverse, and the potential between the platinum indicator electrode and saturated calomel electrode is measured and plotted against the volume of the titrant added, a sharp jump in potential is observed at the end-point, corresponding to the formation and precipitation of mercury molybdate, $HgO.MoO_3$.

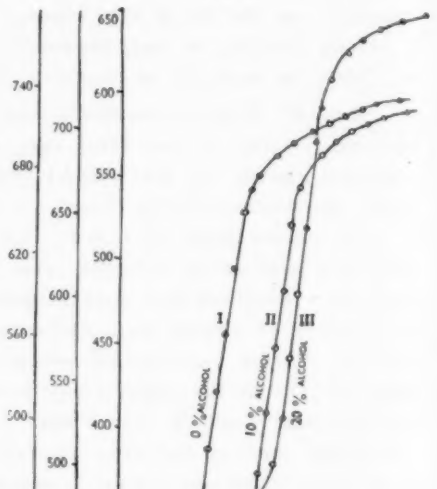
The curves are symmetrical on both sides of the equivalence point and the results are concordant and accurate. The addition of alcohol up to 20% has, however, no effect on the end-point or on the nature of the curves. In the vicinity of the end-point, the sol begins to coagulate and the equivalence point can be visually detected by the coagulation point of mercury molybdate. The reverse titrations (Fig. 2) provide more concordant and accurate results than the direct titrations (Fig. 1). The jump in potential is more marked in the reverse case. Reverse titrations may be recommended for the potentiometric estimation of Hg^{II} as mercury molybdate in highly acidic medium (p_H 1.4 to 2).

FIG. 1



M/10-Na_2MoO_4 *added (c.c) to* 20 *c.c. of* *M*/50-$Hg(NO_3)_2$.

FIG. 2



M/5-$Hg(NO_3)_2$ *added (c.c.) to* 20 *c.c. of* *M*/40-Na_2MoO_4.

The analytical work on the composition of mercury molybdate is under investigation and the results would be communicated shortly.

Thanks are due to Dr. S. Ghosh, D.Sc., F.R.I.C., F.N.I , Head of the Department of Chemistry, University of Allahabad, for his kind help.

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ON THE USE OF POTASSIUM HYDROXIDE AS A BASE IN ACETONE MEDIUM

By K. A. Latif, M. M. Hossain and M. A. Salam

In effecting the N-alkylation of amides, the usefulness of potassium hydroxide in dry acetone medium as a base was first reported by Pachter and Kloetzel (*J. Amer. Chem. Soc.*, 1952, **74**, 1321) and subsequently by Latif and Sattar (this *Journal*, 1955, **32**, 489). In course of the present investigation, attempts were made to find out the factor behind the effectiveness of 'KOH-acetone' as a base. Using *p* nitroacetanilide, two series of experiments were performed, changing only one parameter at a time (*i.e.*, either the base or the reaction medium), and it was observed that weaker bases like lime, baryta or sodium carbonate were of no use whereas dry sodium ethoxide gave fairly good results (all in acetone medium). On the other hand, using KOH in other ketonic solvent medium, such as *cyclo*hexanone and diacetone alcohol (the latter obviously producing acetone in the medium), fairly good results were obtained (yield 60% and 75% respectively). However, non-polar solvents like benzene, ether, etc. were practically useless.

It has been further observed that 'KOH-acetone' also may be employed successfully for effecting certain base-catalysed reactions where normally sodium and alcohol are used, e.g., in the alkylation (both mono- and di-) of malonic ester, cyanoacetic ester, phenylacetone, etc. At least in the alkylation of phenylacetone, this base has been found to be superior to sodium and alcohol, because in presence of the latter, such an alkylation has been reported to be unsuccessful (Suter and Weston, *J. Amer. Chem. Soc.*, 1942, **64**, 533). Also from the data so far available, it appears that this base can effect condensation between malonic ester and ethylene bromide (Perkin's ring-closure) and malonic ester and benzalacetone (Michael condensation). Further works on these are in progress.

A probable explanation of the effectiveness of the base 'KOH-acetone' may be given as follows:

Acetone is likely to come to equilibrium with its corresponding anion (I) whenever a base is added to it:

$$\underset{}{CH_3.CO.CH_3} + B^- \rightleftharpoons \underset{(I)}{CH_2.CO.CH_2^-} + \underset{(II)}{BH}$$

The equilibrium will, of course, be far to the left. However, if a second compound 'AH' is added, which has at least one H atom more protonic in nature than that of acetone, a reaction will immediately take place, forming the anion (III):

$$CH_3.CO.CH_2^- + AH \rightleftharpoons \underset{}{CH_3.CO.CH_3} + \underset{(III)}{A^-}$$

It is this anion which will react further, depending on the condition.

Ethylation of Malonic Ester using 'KOH-*Acetone' as the Base.*—Freshly distilled malonic ester (8 g., 0.05*M*) was dissolved in 100 c.c. of dry acetone and to this dry powdered KOH (5.6 g., 0.1*M*) was added. The mixture was brought to the reflux temperature of acetone, and ethyl iodide (9.4 g., 06*M*), dissolved in 10 c.c. of dry acetone, was added and the whole mixture was refluxed for 2 hours. The solution was then filtered while hot and the acetone was distilled off. Excess of water was added and the mixture was extracted with ether. The ether was then evaporated off and the residue dried over $CaCl_2$ and distilled under reduced pressure. The bulk of the product distilled at 84°/7 mm, yield 8.2 g. (88%); n_D^{28}1.4103, d_4^{28}0.9903. Calculated value of molecular refraction is 47.08 (Found 47.2).

Reaction with other active methylene compounds were carried out similarly.

Methylation of Phenylacetone.—The experimental procedure was identical as above and the time of reflux was 2 hours; yield 80%; b.p. of the product 78°/5 mm, n_D^{22}1.5084, d_4^{22} 0.9980. Molecular refraction calculated for 1:1-methylphenylacetone is 44.8 (Found 44.2). Semicarbazone, m.p. 172° (agrees with the literature value, *Ann. chim.phys.*, 1907, *viii*, **10**, 362).

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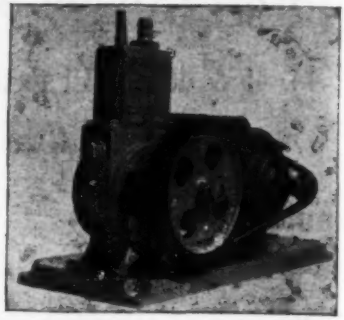

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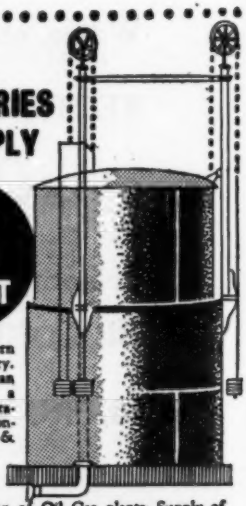

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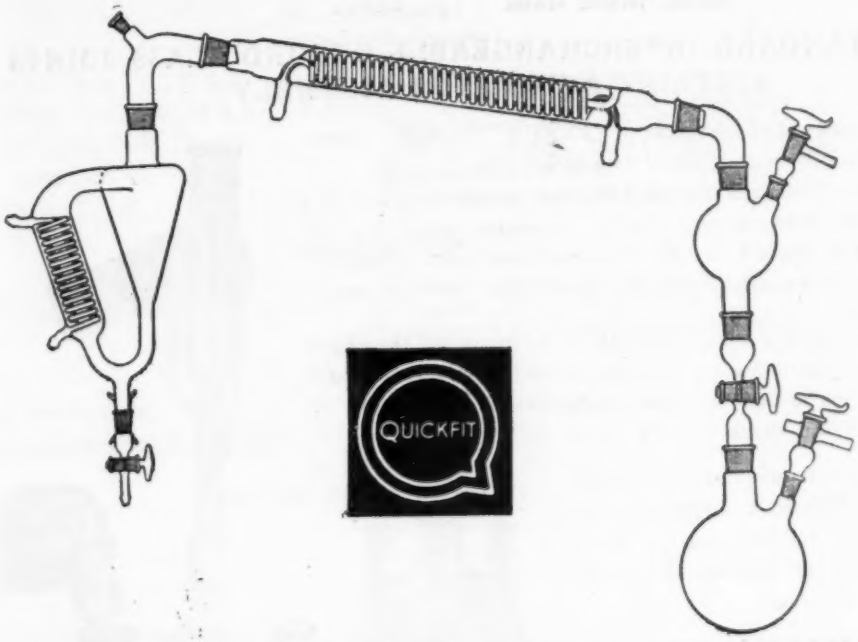

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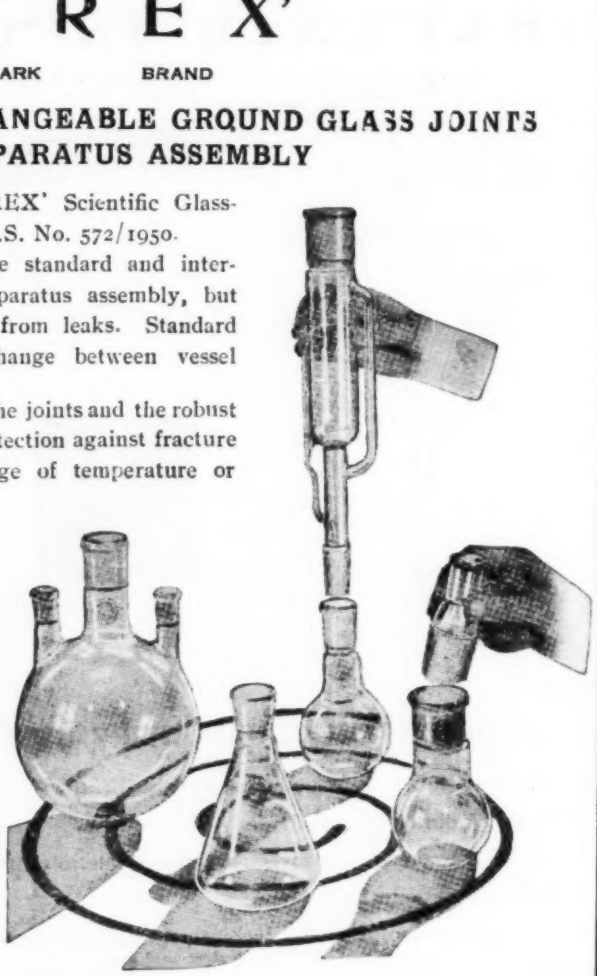

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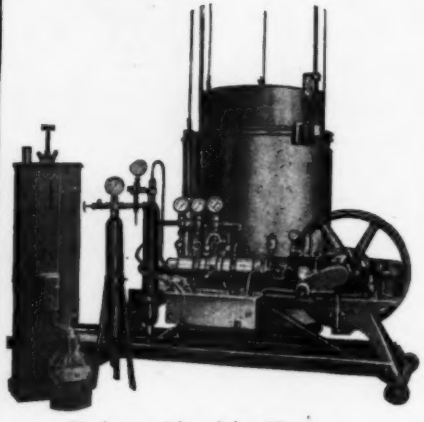

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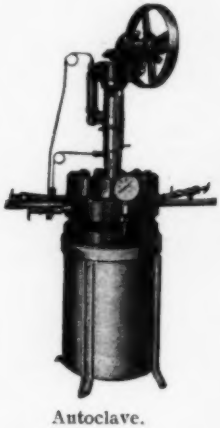

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